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1931-1932.

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BACK NUMBERS OF THE JOURNAL.

Members are notified that the price of back numbers of the JOURNAL has been reduced to a maximum of 10s. 6d. per issue, and that the price for complete volumes (unbound) is £2 2s. A complete set of any ten volumes can be obtained at £20 and Vols. I. to X. also include the Decennial Index covering those volumes.

SPECIAL MEETING.

A Special Meeting of the Institution of Petroleum Technologists will be held on June 14th, 1932, at which it is proposed to exhibit new laboratory apparatus and objects of general interest, and to have presented a series of short papers descriptive of the exhibits. Those desirous of taking part are requested to inform the Secretary of the nature of their exhibit in due course.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS

NOTICES.

The Institution as a body is not responsible for the statements of opinion expressed in any of its publications.

Copyright. Authors of papers and articles are requested to transfer their copyright to the Institution for a period of six months from the date of receipt of the paper. Such transfer should be made in writing when the manuscript is forwarded to the Editor.

Editors are permitted to publish abstracts, providing that acknowledgment is made to The Institution of Petroleum Technologists.

Issue of Journal. The Journal is issued in twelve parts per volume, commencing in January of each year. The Title Page, Table of Contents and Index to each volume are published in the second issue of the succeeding volume.

Members whose subscription is not in arrear receive the Journal free of cost, and additional copies are charged at the rate of 7s. 6d. per part, unless otherwise stated. A member whose subscription is not paid by March 31st of the year for which it is due is considered to be in arrear.

Changes of Address. Members are requested to notify any change of address to the Secretary.

Papers and Articles. Members are invited to submit papers to be read at the General Meetings of the Institution, and are specially asked to forward articles for consideration for publication in the Journal. Diagrams, illustrations, etc., should be suitable for direct photographic reproduction. Authors are informed that all papers, whether for reading or for publication, will be submitted to a referee nominated by the Publication Committee.

Authors of papers published in the Journal are entitled to receive 25 free reprints of their contribution. Further copies may be obtained on payment and orders for these should be sent to the Secretary when the manuscript is forwarded to the Editor. The free reprints do not include any discussion which may be published with the paper, but authors may have such discussion included in their reprints on payment of the additional cost.

Galley proofs of the paper to be read at a General Meeting are available at the time of the meeting, but members desirous of receiving such galley proofs in advance should apply to the Secretary.

Binding of Journals. Members desiring to have their Journals bound in cases should send them, together with a remittance of 5s. 6d. per volume, to Messrs. Speaight & Sons, Ltd., 98, Fetter Lane, London, E.C.4. A charge of 7s. 6d. will be made for binding Vol. 10, 1924. Remittance in all cases must accompany the order.

Abstracts. Abstracts of the more important articles and patent specifications are published with each issue of the Journal, this supplement being paged independently of the transactions. Members and Journal Subscribers desiring to have the Abstracts printed on one side of the paper only can be supplied with these at a charge of 10s. per annum per copy, payable in advance.

Medals. The Redwood Medal is awarded, at the discretion of the Council, to the person who shall have made the most meritorious contribution to petroleum technology, in the form of a paper or papers published in the Journal of the Institution, during two successive sessions, preference being given to original work and to papers which have been read before the Institution and discussed. The award is not confined to members of the Institution and may be withheld if no contribution is considered to be of sufficient merit.

A medal and a prize of five guineas is awarded annually by the Council to that Student Member of the Institution who shall, in their opinion, have presented the best paper during the session.

Benevolent Fund. The Benevolent Fund is intended to aid necessitous persons who are or have been members of the Institution, and their dependent relatives.

The Fund is raised by voluntary annual subscriptions, donations, and bequests, and all contributions should be sent to the Secretary of the Institution at Aldine House, Bedford Street, London, W.C. 2. The Fund is administered by the Council through the Benevolent Fund Committee, and all applications in connection therewith must be made on a special form which can be obtained from the Secretary of the Institution.

Appointments Register. A register of members requiring appointments is kept at the office of the Institution for the convenience of firms requiring the services of petroleum technologists, etc., it being understood that the Institution accepts no responsibility and gives no guarantee.

Library. The Institution's Library may be consulted between the hours of 11 a.m. and 4 p.m. daily. (Saturdays, 11 a.m. to 12 noon.)

Advertisements. Advertisements are inserted in the Journal, and information as to terms, etc., can be obtained from Mr. Thomas Tofts, 301-302, Bank Chambers, 329, High Holborn, W.C.1. (Telephone No. Hol. 4776.)

LIST OF ADVERTISERS.

Members are desired when making enquiries or placing orders with advertisers to mention that they have seen their announcement in the Journal.

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PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Major H. Standish Ball has left for South Africa.

Mr. R. W. L. Bleeck is now in Austria.

Mr. H. C. Carter has returned from Lower Assam.

Mr. A. P. Chamberlain is home from Trinidad.

Mr. G. C. K. Dunsterville has left Holland and is now in Rumania.

Mr. A. J. Engelbach is home from the United States.

Mr. R. E. Fitz-Symons-Bampton is home from Persia.

Mr. W. J. Galloway has returned to Persia.

Mr. S. A. Guest has left France and is now in the Soudan.

Mr. B. R. Jackson is in New York, U.S.A.

Mr. G. D. Jardine has left Burma and is now in Upper Assam.

Mr. H. F. W. Morris has left for India.

Mr. D. W. Treble is home from Iraq.

Mr. J. T. Warde is in Holland.

Major W. H. Goddard has been awarded the Medal and Prize of 25 guineas of the Diesel Engine Users' Association for his paper on "Progress in the Application of the Diesel or Heavy-Oil Engine to Road Transport," read before that Association on November 21st, 1930.

The Secretary would be glad to learn of the whereabouts of the following members :—D. McP. Armstead, C. A. Bauduin, T. E. Beaumont, N. M. Brodie, A. L. Caille, C. R. Clark, E. H. Crush, B. Dvorkovitz, J. W. Elder, P. M. Falconer, W. M. Gray, J. Haker, L. B. Holloway, E. A. Howard, P. Norman Hulme, C. E. Jobling, W. Light, H. Leslie Little, A. MacLean, E. Moscovici, F. A. I. Muntz, R. E. Palmer, Nand Lal Pasi, E. C. Scott, W. E. Shepherd, E. F. H. Spencer, D. Steel, C. M. Stoney, T. C. G. Thorpe, L. J. Truss, R. K. Van Sickle, F. E. G. Watson and S. S. Webb-Bowen.

DINNER CLUB.

The attention of members is drawn to the Dinner Club of the Institution. This Club holds informal dinners after each General Meeting of the Institution and members may invite guests. Those desiring to receive notice of these dinners are requested to inform the Secretary of the Institution.

SMALL ADVERTISEMENTS.

In future the advertisement columns of the Journal will be open for the inclusion of small prepaid advertisements, such as Situations Vacant and Wanted, Patents for Sale and Miscellaneous, at a charge of 1s. 0d. per line of seven words (minimum 4s. 0d.). A charge of 1s. 0d. will be made for the use of a box number. Matter for insertion should be in the hands of the Associate Editor not later than the 12th of the month in which it is desired that the advertisement should appear.

BRITISH STANDARDS INSTITUTION.

During recent years the British Engineering Standards Association has prepared British Standard Specifications, and established British Standards not only for use in the Engineering field, but also for a growing range of materials in the Building, Chemical and Textile industries.

The need for regularising this extension of the original functions of the Association has been under consideration from time to time, and became imperative when the Chemical industry, as a result of a fully representative Conference convened by the Association of British Chemical Manufacturers, invited the Association to widen its scope to include Chemical standardisation generally.

The Building industry also desired a substantial extension of the work of standardisation within that industry, and urged that the title of the Association should be more in conformity with the wideness of its scope.

At the Imperial Conference held in October, 1930, the desire was expressed that there should be a single centralised National Standardising Body in each of the countries forming the British Empire.

It was therefore decided to re-organise the work of the Association into four main Divisions of equal standing, responsible for the preparation of British Standard Specifications in the Engineering, Chemical, Building and Textile industries, each of the Divisions being under the control of a representative Divisional Council.

The Council, therefore, after securing the approval of the members of the Association, applied for, and have been granted, a Supplemental Royal Charter, authorising these changes.

In future the name of the Association will be the "British Standards Institution," and its activities will be under the control of a General Council which will have under it the four Divisional Councils. The work of the Engineering Division will, as before, be delegated to Industry Committees dealing with the main branches of the Engineering industry, such as civil engineering, mechanical engineering, electrical engineering, etc., and will, of course for a time, represent the larger portion of the Institution's activities.

The great development in the standardising movement, which has taken place since the first Committee was set up by the Institution of Civil Engineers in 1901 as the Engineering Standards Committee, is a clear indication that industry as a whole has increasingly recognised the economic value of the work. There are now 600 Committees and over 400 published British Standard Specifications. The term "British Standard" has been registered by the Institution as its standardisation mark. The Institution is not a profit making concern, and apart from the grants received from the Government and the amount derived from the sale of its publications, it has to look to the associated industries for the funds necessary to carry on the work. Every British firm in these industries is eligible to become a member of the Institution at a nominal fee.

NOMINATIONS FOR MEMBERSHIP OF THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The following have been nominated for membership of the Institution of Petroleum Technologists and their Application Forms may be seen at the Offices of the Institution:—

	Proposed by	Seconded by
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MOORE, Charles Frederick Carre, Geologist (Trans. from Stud.), c/o The Burmah Oil Co., Badorpurghat, Sylhat, Upper Assam, India	H. M. Sale.	P. Evans.
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As Associate:—		
DYKES, Herbert James, Accountant, "Matlock," 69, Holmdene Avenue, Herne Hill, London, S.E. 24	C. Dalley.	R. R. Tweed.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE ONE HUNDRED AND THIRTY-EIGHTH GENERAL MEETING of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, Adelphi, London, on Tuesday, November 10, 1931, Mr. JAMES KEWLEY, M.A., F.I.C., F.C.S., President, occupying the Chair.

The Secretary read the list of candidates nominated for election, and the following list of members elected :—

As Members.—Cyril Harding Sprake, Edward Thomas.

As Associate Members.—Ralph John Bressey, Harry William Humberstone, Herbert Corner Reynard.

Transferred to Associate Member.—Joseph Edwin Walker.

As Associate.—Reginald Arthur Nixon.

The following paper was read by the author :—

The Dilution Theory of Detonation.

A NOVEL MATHEMATICAL STUDY OF THE AUTO-IGNITION THEORY OF PINKING IN THE LIGHT OF CERTAIN RECENT DEVELOPMENTS.

By I. A. J. DUFF, B.A., A.M.Inst.C.E.

SUMMARY.

Evidence is offered that the cause of pinking is an interaction of a small quantity of the fuel and oxygen of the charge as described by Callendar, Mardles and King[1] and that the increase of knocking tendency varies directly with the concentration of oxygen in the charge ; as no equally simple law applies to all classes of anti-knock fuels the assumption is made, that a small portion of the oxygen content of the charge is reactive but only during the latter part of the compression stroke and first portion of the firing period and that this combines with any of the pro-knock fuel with which its active molecules come in contact.

The products are assumed to play a part which will be dealt with shortly.

The phenomenon of delay action or " wait time " in the ignition of charges adiabatically compressed above a certain point described by Tizard and Pye[2] is explained and employed as follows :—

It is considered that above a certain limiting temperature the products postulated above act in some way as " irritants " causing more or less rapid temperature rise until a point is reached at which ignition sets in. Making a few simple and justifiable assumptions a mathematical expression is developed for several different types of anti-knock, connecting the improvement of engine test with the amount of diluent or anti-knock present.

[1] *Aero. Res. Rep.*, 1062, Dec., 1926.
[2] *Phil. Mag.*, 1922, **44** (VI), 79.

The figures thus derived theoretically are found to fit those determined practically by several different observers at various times, places, and on different engines, with an accuracy equalling or surpassing the experimental error, in the case of fifteen different combinations of pro- and anti-knock (which are all that have yet been studied).

Furthermore, if the theory itself is accepted an explanation is at once available for a large body of facts which have hitherto been baffling and contradictory; and insight into the scheme of the reactions leading to and causing the pink and its actual mechanism can be obtained without any difficulty.

Introduction.

Recent work in the testing laboratories of the great oil firms and elsewhere has compiled an enormous quantity of facts bearing on the subject of pinking; very often as yet uncorrelated to any known chain of causation.

The object of this paper is to supply a framework in the shape of a working hypothesis into which as many as possible of the facts can be fitted without distorting either the framework or the fact.

The basic idea of the hypothesis—self-ignition of a modicum of the charge under certain conditions—is no new one as it was put forward by Ricardo in 1924, but no clear explanation of the rationale was put forward then or later, and subsequent work has, if anything, tended to discredit and overlay the idea.

More recent work by Callendar, Mardles and King (1926), taken in conjunction with Ricardo's work (1924), and experimental work due to the Michigan Laboratory (1928-9), Maxwell and Wheeler (1927-8) and the Anglo-Persian Oil Co.'s Research Laboratory and Engine Research Branch have supplied the links missing in 1924, and it is now possible to offer a theory which fits ascertained facts so closely that it may even be deemed worthy of consideration as a fundamental explanation.

The hypothesis is, in brief, that every fuel has an actual ignition temperature below which oxidation is fairly slow, but above which a flame forms and propagates rapidly throughout a mixture; that ignition at this temperature arises from neuclei which in the case of pro-knocks are probably the peroxides ("irritants") discovered by Callendar, Mardles and King; that these irritants are formed during the latter part of the compression stroke and cause local actions and rise of temperature; and that if this rise reaches the ignition temperature in the still unburnt part of the charge the latter ignites with a more or less sudden rise in temperature and pressure, causing the emission of a wave pulse of extremely sudden increase of pressure (almost square fronted), the impact of which on the walls causes the "pink."

The hypothesis as thus stated has nothing novel as it is a condensation product of the work of the authorities quoted above and others, all of whose work agreed in the main experimentally, though their interpretations of the results often did not.

The novelty of the present paper is that by making some perfectly reasonable assumptions from these results it has been possible to correlate the quantitative work of many different workers on engine testing figures and to develop a mathematical theory into which the known facts fit comfortably.

As a rule the assumptions of which use is made in the course of the argument are based on some practical observation often made in a different connection.

The two intangible conceptions of which use has to be made are : " active " oxygen, and the effect of " irritant " in causing a rise in temperature leading to auto-ignition.

The first is analogous to, or possibly actually, the " active mass " which is usually postulated in physical chemistry to explain non-instantaneous reactions ; the second is similar to the phenomena of spontaneous combustion in its effect.

The Dilution Theory.

Tizard and Pye found that if an explosive mixture were compressed sharply so that it were heated by the almost adiabatic compression, the temperature would continue to rise and it would ignite itself after a short period (the " wait time "), which varied from product to product. The length of the period also varied with the temperature to which the gas mixture had been raised by the compression.

For practically every chemical reaction there is a critical temperature below which action is much retarded (almost non-existent) and a few degrees above which it proceeds readily. There seems no *a priori* reason why the temperature at which combustion actually begins and sweeps through a mixture (hereafter called ignition temperature) should not be such a critical temperature controlling the oxidation of hydrocarbons and other combustible substances. Below the ignition temperature oxidation will proceed more or less slowly, and if the heat so produced accumulates the temperature will rise after a period of time (" wait time ") to the ignition temperature, when the reaction will complete itself rapidly (*c.f.* Walker).[3]

The " self ignition temperature " observations made by Moore,[4] Ricardo and other observers will not be the same as the ignition temperature, as the observations really were made of the lowest

[3] *Physical Chemistry*, 1922, pp. 292, 293.
[4] *J.S.C.I.*, 1917, **36**, 109.

temperature from which after the corresponding "wait time" the mixture would ignite and this would vary from observer to observer according to the physical constants of the apparatus.

Experiments on carbon disulphide and other vapours however seem to indicate that such an ignition temperature exists, and that it is practically constant for each product over the combustible mixture range. Tizard and Pye also noted that when self-ignition experiments were carried out under comparable conditions on various products the "wait time" varied from product to product.

Experiments by Callendar, Mardles and King showed definitely that when a mixture of hydrocarbon and air was passed through a tube heated to a certain temperature slow reaction took place, and beside the ordinary partial combustion products of CO_2, aldehydes and ketones, etc., a very small quantity of peroxides was formed which detonated in a hotter part of the tube and whose presence could be shown by the usual reaction.

These peroxides are exothermic in their formation and decomposition, and their operation as nuclei of reaction would explain very nicely the observations of Dixon and others[5] that ignition starts from a number of nucleoid centres.

It is therefore assumed for the subsequent treatment that the length of the "wait time" in Tizard and Pye's determinations is conditioned by the greater or lesser amount of the peroxide formed, which acts as a local "irritant" causing the temperature of the reaction charge to rise by furthering local reactions until the general temperature reaches that of ignition, when the whole charge ignites more or less together.

If the hydrocarbon forms a lot (comparatively) of the irritant the action will be from many points, the temperature rise rapid and the wait time short; if only a little the reaction will be slow and the wait time longer.

Methods of engine test have been described exhaustively in many articles,[6] and, most valuably, since all the latest details of operation are given, in the symposium printed at length in *The Journal of the Society of Automotive Engineers*,[7] and by Stansfield and Thole.[8]

The important point concerned in all these different methods of test is that for the purposes of this study it does not matter under what system the engine test was taken provided only that it

[5] Dixon, Bradshaw & Campbell, *J.C.S.*, 1914, **105**, 2027; Dixon & Crofts, *J.C.S.*, 1914, **105**, 2036.

[6] Notably *National Petroleum News*, Jan. 15, 1930, p. 61, Brown & Zuck, and *Rept. of Empire Motor Fuels Comm.*, 1924.

[7] April, 1930, **26**, 479.

[8] *Engineering*, 1930, **130**, 468.

complied satisfactorily with its own rules and the results can be stated in comparable units.

Ricardo states[9] that the effect of adding 3·08 per cent. of oxygen to the air constituent of a hydrocarbon mixture is to lower the engine test by as much as the addition of 13·05 per cent. of the inert diluent nitrogen raises it, but does not comment further on the observation. It is, however, to be noticed that these additions raise and lower the partial pressure of the oxygen from normal by an equal amount, and therefore the change in engine test of a hydrocarbon mixture varies directly with the partial pressure of the oxygen component.

It is also a matter of general observation that additions of non-knocking spirits raise the engine test of pro-knock spirits, and from this a deduction can be made that the knocking effect depends in some simple manner on the "active masses" of oxygen and pro-knock present.

The assumption is made that the same effect takes place in the engine as in Callendar, Mardles and King's experiments, namely, that above a certain temperature the oxygen and pro-knock react in small proportions, forming "irritants" which cause local action, heating part of the mixture to its self-ignition temperature and igniting it by nucleoid action.

In the case of a mixed fuel whose components have different ignition temperatures the ignition temperature should be approximately that of the lower constituent until the concentration of the latter becomes so small that the local actions which lead to ignition at the lower temperature scarcely reinforce each other when the ignition temperature will steadily rise to that of the higher constituent.[10]

During the course of the compression stroke of an I.C. engine the temperature is reached at which the irritant can form. From that instant to the end of the combustion or the "pink," during the period which will hereafter be called the reaction time, the "irritant" is considered to be inaugurating local action and raising the temperature, over and above the other rise due to the compression by the piston and/or the burning of the first part of the charge. All these rises in temperature add together till the result equals the ignition temperature. If the temperature of any unburnt part of the charge reaches the ignition temperature the charge thereupon ignites from the irritant as nuclei, and general ignition throughout the remainder will ensue.

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[9] *Rept. of Empire Motor Fuels Comm.*, 1924, 329, 331.

[10] *J. Inst. Petr. Techn.*, 1927, **13**, 264.

On this assumption naturally the pressure rise in the "pinked" or self-ignited part of the charge would be much more sudden if the mixture is ignited from many nuclei than if from few: *i.e.*, benzol (which Callendar, Mardles and King showed not to form irritants perceptibly) should not preignite in ordinary circumstances; whereas paraffins (*e.g.*, nonane) should give an ignition wave like a true detonation from the larger quantity of irritant they form.

The method of measuring "pink" by the Midgley pin consists really in delivering a standard amount of impulse energy to the diaphragm or in ensuring that a small constant proportion of the charge detonates.

Let τ be the "wait time" between the moment when the formation of irritant begins and the moment when the ignition temperature is reached. (This in any compression ending in self-ignition, such as the bomb experiments.)

Let T be the reaction time in the I.C. engine between commencement of formation of irritant and either the end of combustion or "pink."

Let a mixture of x of anti-knock spirit or diluent, *i.e.*, benzol, alcohol, etc., and (1—x) of pro-knock spirit be taken for engine test.

When this mixture is carburetted and put through the standard cycle, let it form q of knock-inducing "irritants," where q is the fraction of the amount which would be formed were pure pro-knock spirit used and put through the same cycle.

It can be shown by the use of the law of mass action that assuming that the quantity of oxygen present is substantially unchanged during the formation of the irritants

$$q=(1-x) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

We are entitled to make this assumption for two experimental reasons: (1) The amount of irritant formed was found to be very small in the experiments of Callendar, Mardles and King, and (2) a charge which has been put through such a compression cycle shows no great change of oxygen content.

Let p_θ, v_θ, α_θ be the pressure, volume and absolute temperature of a charge at the beginning of a compression stroke, and p, v, α, that of the charge at the end of compression.

In view of the care taken to keep experimental conditions constant during the course of an engine test it is fair to assume the law of compression in a test engine to be pv^n=constant, where n varies from engine to engine, but is somewhere about 1·3.

Then, since $pv^n = C$

and $pv = R\alpha$ (ordinary gas law)

$$(\alpha - \alpha_0) = \frac{C}{R}\left(\frac{1}{v^{n-1}} - \frac{1}{v_0^{n-1}}\right)$$

$$\text{or } \alpha - \alpha_0 = K_0\left\{\frac{v_0^{n-1}}{v^{n-1}} - 1\right\} \quad \ldots\ldots\ldots\ldots\ldots (2)$$

$$\text{where } K_0 = \frac{C}{Rv_0^{n-1}}$$

Let y be the improvement of engine test of the mixture over pro-knock, $= \dfrac{\text{H.U.C. mixture} - \text{H.U.C. pro-knock}}{\text{H.U.C. pro-knock}}$

α be the end-of-compression temperature of the mixture at its H.U.C. (p, v, α)

α_1 be the end-of-compression temperature of the pro-knock at its H.U.C. (p_1, v_1, α_1)

y, the improvement in engine test, can be determined in terms of the change in end-of-compression temperature, for

$$y = \frac{\text{H.U.C. mixture} - \text{H.U.C. pro-knock}}{\text{H.U.C. pro-knock}}$$

$$= \frac{\dfrac{v_0}{v} - \dfrac{v_0^*}{v_1}}{\dfrac{v_0}{v_1}}$$

$$\text{or } \frac{v_1}{v} = (1+y) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

From (2)

$$\alpha - \alpha_1 = K_1\left\{\left(\frac{v_1}{v}\right)^{n-1} - 1\right\}$$

whence $\alpha - \alpha_1 = K_1[(1+y)^{n-1} - 1] \quad \ldots\ldots\ldots\ldots\ldots (4)$

Let β be the self-ignition temperature of the mixture, and t the time between the beginning of formation of irritant and when ignition is complete at the point of origin of the pink.

It is assumed that the rise of temperature during the reaction time (T) due to the action of the irritants is a function of q, and T the time of action of q.

Now T and q are variables independent of each other since the operator can vary either while keeping the other constant,

* v and v_1 are "characteristic volumes." If v_s is the swept volume and v_c the clearance volume corresponding to p, v, α: $\dfrac{v_s + v_c}{v_c} = \dfrac{v_0}{v}$ when the volume originally taken has been compressed to v.

by running the engine at a different speed or by altering the proportions of pro- and anti-knock in the mixture.

In engine testing a and q are the controlled variables, a being the dependent variable.

If x increases by dx, q decreases by dq, and a increases by da.

Since it has been assumed that arrival at the (Constant) Self Ignition Temperature is the cause of the pink, the increase in compression temperature da must be offset by a corresponding reduction in the chemical rise in temperature $K_2T\,dq$

or
$$da^* + K_2T\,dq = 0 \quad \ldots\ldots\ldots\ldots\ldots (5)$$

If T can be expressed in terms of a or of q expression (5) can be integrated.

Case 1.—A diluent anti-knock is used which does not form irritants nor combine appreciably with oxygen below its combustion temperature.

It can be shown (Appendix B) that when the self-ignition of such a compressed charge takes place from a given temperature, the "wait time" τ varies inversely with the proportionate amount of irritant present or

$$q\,\tau = C_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

From (5) $da + K_2T\,dq = 0$

and from (6) $q\,\tau = C_2$,

and at the critical knocking point

$$\tau = T\dagger$$

substituting accordingly,

$$\frac{da}{dq} + \frac{K_2}{q} = 0$$

Integrating
$$a = K_2 \log \frac{1}{q} + C_2$$

but when $q = 1$ (pro-knock spirit)

$$a_1 = K_2\,0 + C_2$$

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* The heat release during combustion is experimentally the same for all usual fuels and the rate of flame transmission is of the same order; it is therefore assumed that the pressure rise is approximately the same, hence that the temperature rise during combustion compression is the same. Whence a may include the combustion compression temperature rise without upsetting the argument.

† The "wait time" must equal the reaction time at the reaction temperature for critical knock. If τ were greater than t the unexpended portion of the charge would not self-ignite till it were lit by the advancing flame front (knockless operation), and if τ were smaller than t the knock would have occurred earlier, *i.e.*, would be larger than the standard. Also $t = T$ for critical knock operation.

$$\text{or } a - a_1 = K_2 \log \frac{1}{q} \quad \ldots\ldots (7)$$

$$\text{Since} \qquad q = (1-x) \quad \ldots\ldots (1)$$

$$\text{and } a - a_1 = K_1 [(1+y)^{n-1} - 1] \quad \ldots\ldots (4)$$

$$(1+y)^{n-1} - 1 = \frac{K_2}{K_1} \log \frac{1}{(1-x)}$$

$$= K_4 \log \frac{1}{(1-x)} \quad \ldots\ldots (8)$$

$$\text{or } y = \left\{ 1 + K_4 \log \frac{1}{1-x} \right\}^{\frac{1}{n-1}} - 1 \quad \ldots\ldots (9)$$

Alcohol and benzol, which from chemical considerations comply with the requirements for Case 1 (Callendar, Mardles and King, *loc. cit*) give engine test curves corresponding exactly to the log curves derived theoretically above up to about 60 per cent. additions.

Above this the anti-knock effect is considerably better than the log curve, which is due to the assumptions being no longer true in two particulars.

(1) β begins to move up to the higher ignition temperature of the anti-knock as the concentration of anti-knock rises higher, which permits a and hence y to increase itself with qT kept constant.

(2) The diluent begins to attack oxygen though it does not form irritants, thus reducing the amount of active oxygen available for the formation of q.

Neither alcohol nor benzene has an H.U.C. in the true sense of the term.

Case 2.—High knocking compounds such as iso-octane and naphthenes.

It is assumed that these, like the paraffins, form irritants, but not so readily, as their H.U.C.'s though true ones are considerably higher than those of the paraffins.

Let the formation rate of irritants in the diluent be (1 — m) (a fraction), where that of the pro-knock = 1.

As before,

$$a - a_1 = K \log \frac{1}{q} \quad \ldots\ldots (7)$$

but when x diluent is added, q is now the combined quantity

(1 — x) due to pro-knock
(1 — m)x due to anti-knock,

$$\text{or } q = 1 - mx,$$

$$\text{and } (1+y)^{n-1} - 1 = K_4 \log \frac{1}{1-mx} \quad \ldots\ldots (10)$$

The two cases given above are special cases, since the "wait time" is determined entirely by the pro-knock constituents—the anti-knocks being demonstrably (Callendar, Mardles and King, *loc. cit.*) practically inert to oxygen up to the ignition temperature.

There is, however, a large class of anti-knocks usually characterised by unsaturated valencies (double or triple bonds) and which are easily oxidised or chlorinated. These are not indifferent to "active oxygen" and any which escapes seizure by the pro-knock will be taken up by the anti-knock, so that the quantity of irritant q formed will now be a constant, but the irritating power of the anti-knock product is not so great by hypothesis and may be rated at d times that of the pro-knock irritant.†

The quantity q_x formed when a blend of x diluent to (1—x) pro-knock is used, stated in terms of pro-knock irritant, may be shown by the law of mass action to be a simple linear function of x.

(1 — x) pro-knock contribution,

d.x anti-knock contribution stated in terms of pro-knock.

$$q_x = (1 - g.x) \text{ (say)} \S \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

Case 3.—Assume the "wait time" to be constant for all mixtures at the same temperature,

i.e., τ_1 (pure pro-knock) $= \tau_2$ (pure anti-knock) $= \tau_x$ (mixture)

$$d\alpha + K_2 T\, dq = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5).$$

$$\therefore \frac{d\alpha}{dx} + K_2 T \frac{dq}{dx} = 0.$$

$$\tau_1 = \tau_2 = \tau_x = T = \text{constant}^*\ ;\ q_x = (1 - gx)$$

$$\therefore \alpha - \alpha_1 = K_2 T g x$$

or from (4) $(1 + y)^{n-1} - 1 = K_3 x$

$$y = (1 + K_3 g x)^{\frac{1}{n-1}} - 1$$

which is to all intents and purposes for the engine tests under consideration

$$y = \frac{K_6}{n-1} x \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

Inspection of the constant K_6 shows that the slope of the curve (*i.e.*, the goodness of the anti-knock) depends on the size of d, the anti-knock virulence fraction.

If d were greater than 1 the product would act as a straight line pro-knock (*e.g.*, decalin).

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* For critical operation the compression ratio is increased till τ_x does equal T.

†§ Where d is a constant, < 1 and $g = (1 - d)$.

The initial effect of these easily oxidisable anti-knocks is often very striking in virtue of their combined diluent and oxygen grabbing qualities.

For example, the olefines have mild oxygen grabbing affinities and a moderate slope, but such compounds as tetraethyl lead toluidine and iron carbonyl, with great affinities for "active" oxygen, have immense effects for a small addition.

The effect is considered to be that the greater proportion of the "active" oxygen is seized and rendered harmless as far as forming irritants is concerned, which is equivalent to reducing the effective partial pressure of the oxygen with respect to the pro-knock, so that the diluent effect is enhanced by the oxygen grabbing effect.[11]

If further it is assumed that at high temperatures the avidity of tetraethyl lead for active oxygen increases at a faster rate than that of the pro-knock, a complete explanation of the improved effect of tetraethyl lead at high operating temperatures is possible.

Maxwell and Wheeler[12] point out that tetraethyl lead does not act as an anti-knock unless decomposed first; *i.e.*, when the temperature of a gas is raised purely by explosion, as in their bomb experiments there is not sufficient time for the lead smoke to form and steal oxygen. (The compression is equivalent in that case to a piston moving at some 200 ft. per sec.)

The slower compression of the piston of an engine at (say) 1000–2000 ft. per minute gives the decomposition time to take place and the oxygen grabbing effect time to happen. The effect of heated jackets is to enable the tetraethyl lead to reach its decomposition point earlier in the cycle and thus to have a greater effect. (Probably a greater percentage of the tetraethyl lead is decomposed in time to be active; if this is so, a saturation effect for each per cent. of tetraethyl lead, with increase in temperature, should be noticeable.)

There is a good deal of experimental evidence in favour of this: (1) Tetraethyl lead was found to *lower* the self-ignition temperature of its mixtures on the whole, *i.e.*, its avidity becomes infinite at a lower temperature than that of the pro-knock. (2) Several observers have stated that tetraethyl lead has no knock extinguishing effect unless and until it were decomposed by heat. (3) An oxygen carrier counters the effect of tetraethyl lead. (4) The curves of engine test for most or all of the olefines, diolefines, etc., the small dilutions of toluidine, tetraethyl lead, iron carbonyl and the like all show experimentally the straight line curve demanded by this theory; in fact, the straight line applies to most of the easily oxidisable diluents.

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[11] *J. Inst. Petr. Techn.*, 1927, **13**, 281.

[12] *J. Inst. Petr. Techn.*, 1929, **15**, 408-420.

Case 4.—Assume the "wait time" to be a function of the dilution, say

$$(u + hx) \quad \ldots\ldots (13)$$

q_x is as previously derived $(1 - gx)$ in terms of pro-knock (11)

As before,

$$da + K_2 T\, dq = 0 \quad \ldots\ldots (5)$$

$$\therefore \frac{da}{dx} + K_2 T \frac{dq}{dx} = 0$$

For limiting knock

$$T = \tau = (u + hx) \quad \ldots\ldots (13)$$

$$q_x = (1 - gx) \quad \ldots\ldots (11)$$

Whence $\frac{da}{dx} + K_2(u + hx)(-g) = 0$

And by integrating and substituting for the constant of integration

$$(1 + y)^{n-1} - 1 = K_2 ugx + K_2 hg\frac{x^2}{2} \quad \ldots\ldots (14)$$

The Effect of an Altering β.

The ignition temperature β has till now been taken as constant throughout the range and, as pointed out, the equations are vitiated in their application above about 70 per cent. in consequence of this; it is impossible to give an exact treatment of this quantity owing to a total lack of reliable and consistent determinations, so the writer will just content himself with indicating the effect.

There is a continuous curve of some shape connecting the rise of ignition temperature and increase of x, and this can be expressed as some kind of Fourier series in x.

As differentiation and integration of this in the equations only gives an addition of a quantity whose curve echoes the I.T./x curve, it can be assumed with a fair degree of safety that the curve at the top end will contain an aberration corresponding in tenor to the I.T./x curve.

Thus benzene shows a big rise of I.T. with heptane and a large and otherwise unaccountable increase of engine test in practice over theory. Heptane and iso-octane, whose I.T.'s are much nearer together, do not show this rise of I.T. to the same extent, and the theoretical and practical determinations coincide from 0 to 100 per cent; and tetraethyl lead, with its drooping I.T. curve, is said to fall off considerably at the higher concentrations in engine test.

The theory as a whole also accounts for the previously very puzzling fact that additions of CS_2 up to 50 per cent. give anti-knock effects, whereas greater give pro-knock and pre-ignition effects; for the addition of small quantities of CS_2 will have a diluent

effect and take up "active" oxygen and raise the H.U.C. of the mixture as long as the I.T. of the mixture is not thereby lowered. As soon as that begins to travel downwards the engine test curve will pass through a maximum and fall rapidly as soon as the fall in β overpowers the dilution effect (and oxygen stealing effect).

Curves based on Case 4 equations fit the behaviour of cracked spirit, cyclohexene, tetramethylethylene, etc., very closely.

Objection may be taken to this theory from the very simplicity of its assumptions, since no apparent cognisance is taken of the multifarious variables connected with the operation of an engine; but from a very early date in the history of engine tests it has been known that tests are only self-consistent and repeatable as long as such variables as radiation and conduction, volumetric efficiency, timing, rate of cooling, etc., all of which make a considerable difference to the H.U.C. of a spirit in any given engine, are kept as constant as is experimentally possible, and a little consideration shows that the conditions of a practical engine test must tend to cut down the number of variables just as the method adopted in obtaining the equations (by differentiation) eliminates the variables which are so carefully kept constant in practice.

The theory, as propounded, has, moreover, a complete explanation to offer for many widely scattered facts besides those to which reference has been made above.

For example, the reason a heated inlet system lowers the H.U.C. of a spirit, the value of good engine head design, the value of aluminium for heads and pistons, the reason amyl nitrite (an oxygen carrier) is pro-knock can all be explained from the theory very comfortably, and pre-ignition and pinking no longer need to be considered as two separate things, but rather as two separate manifestations (in different phases of the cycle) of the same phenomenon.

Turbulence is seen to have its chief value as an anti-knock agent in that it cuts down the combustion time (*i.e.*, it shortens T) and ensures that the mass heats together with no local overheating. It also makes it much less possible for a clearcut stationary wave to form (see below.)[13]

The equation $\alpha + \mathrm{K.f}\,(q, T,) = \beta\dagger$

will be found to contain in its members the sufficient explanation of every known method of altering the knock value of a spirit.

(1) α. A reduction of α for any given C.R. will increase the H.U.C.R., since the C.R. may be increased till α returns to its value to satisfy the equation. The methods of reducing α are:

(a) Cooling the charge of air before it enters the cylinder.

† *I.e.*, compression temp. + rise in temp. due to chemical action = S.I.T.

[13] *J. Inst. Petr. Techn.*, 1930, **16**, 756-776

(*b*) Not permitting addition of heat at any point, *e.g.*, by radiant masses or hot spots.

(*c*) High turbulence (Stops local overheating and cools charge during compression by loss to cylinder walls—but, of course, this is reversed if the cylinder walls are in such a condition that they would heat the charge.)

(*d*) Use of fuels of high sp. ht. and/or high latent heat of vaporisation (*e.g.*, alcohol).

(*e*) Addition of indifferent fluids of high sp. ht. and latent heat ; —water cools the charge by evaporation.

Steam or atmospheric humidity should have relatively little effect compared to liquid water as its effect is largely diluent only.

(*f*) Good wall conduction—*e.g.*, aluminium heads and pistons in a turbulent engine : this may be reversed if heating of the walls occur.

(*g*) Spark alteration. α is the highest temperature attained by the action of compressions of the piston and the burning of the first part of the charge ; and the shape of the combustion pressure rise curve from the indicator diagram should be useful information on this point. A fuel which gets a very different indicator pressure diagram on spark alteration should be much more sensitive to spark. An important practical point is involved in this question of the reduction of α ; although tests of a spirit can be made self consistent on any modern engine, it does not in the least follow that another engine of the same make will agree as to the match or the placing in order of several blends of different base spirits—in fact this should *not* be so in the case of any anti-knock with a big temperature improvement, such as tetraethyl lead unless the α's of each engine are the same ; *i.e.*, unless each engine puts the blends at the same absolute C.R., and has the same amount of turbulence in the same shape and size of combustion chamber made of the same metal in the same condition.

As even the same make of engine varies in these respects, trouble is to be expected in trying to match dissimilar types of anti-knock when one of them has a temperature effect widely apart from the other.

The incidence of the trouble will be in the oxygen grabbers, such as cracked spirit, tetraethyl lead, etc., where the chemical affinity of the anti-knock for the " active " oxygen would alter with an alteration of temperature ; the pure diluents such as benzene, alcohol, and possibly iso-octane would tend not to give any such trouble.

(2) K varies from engine to engine.

K.f(q, T,) is a thermometric rise, and anything tending to remove heat as it accumulates during the "wait time" will lower K and raise the possible a.

(3) q can be reduced by displacement of pro-knock by any non-q-forming anti-knock, *e.g.*, benzol, or by partial or complete removal of the "active" oxygen partner by (a) dilution of the oxygen with inert diluents or (b) action of oxygen stealers such as tetraethyl lead.

It is doubted whether, once formed, q can be decomposed without the undesired temperature rise, as decompositions of peroxides are, generally speaking, exothermic.

(4) T, the reaction time, can be shortened by speeding the engine up which is known to eliminate a knock.

On the other hand, really fast running raises a, as less time is afforded for cooling during compression, and this may actually cause pre-ignitions in even such respectable fuels as benzol!

(4A) τ, which = T at critical knock, can be increased by lowering the "virulence" of the irritant.

(5) β It has been known for a long time that the ignition temperature of a fuel had a lot to do with the H.U.C. value, though studied as S.I.T.s the results were obscure because of the many variables involved.

A high β (benzol) gave a good anti-knock effect; a low one (ether) a bad one; but lowering the β of a mixture did not always mean a worse engine test (ethyl).

This can be easily understood if it is studied in conjunction with q—if the f(q, T,) term decreases faster than the β term a must increase.

The effect of a diluent at high jacket temperatures can be seen to be explained by the combined action of an actual increase in a for a given C.R. and a possible change in the oxygen grabbing effect of the diluent.

The combined effect of the two may be positive, zero, or negative in the net effect on the engine test.

Some extremely important work was carried out by Maxwell and Wheeler on transmission of flames in bomb explosions and the location of the probable source of the pink; and this survey would not be complete without a consideration of their results and their bearing on the theory presented in this paper. Their observations provide important information as to the actual source of the pink in an engine.

It will have been noticed that the study given above has only dealt with the engine test evidence that the genesis of the pink is a

point of auto-ignition, but has not considered the location of the actual effect, except that it seems to show that the beginning of the trouble is on or in advance of the flame front.

Maxwell and Wheeler found that for pinking conditions the flame front suddenly became vibratory, accelerated, and the pink occurred just before or when the flame front reached the end wall, whereupon an incandescent flash passed backwards through the path of the flame. In certain conditions the existence of auto-ignitions was detected by the photos, ahead of the flame front but the flame was not usually pinking under those conditions.

It was observed that flames with a long after-burning (*i.e.*, with a considerable depth of flame) tended not to pink; whereas those in which the reaction completed quickly conduced to pinking.

The general conditions for a singing flame are exactly the same as those for any other sustained vibration—*i.e.*, a condition of "negative resistance" must exist.

As, however, the materials of a flame cannot be put through a rapid cyclical change the flame must have translation through space at varying speeds, or if it is to be a stationary singing flame the combustible must have a varying rate of flow; *i.e.*, pressure varied by the flame (the standard method of producing a singing flame).

The formation of a vibrating flame is as follows:—

It is well known that the speed of a flame in a combustible mixture increases with an adiabatic increase of pressure at the flame front (see note at end of this section). Assume a flame front progressing uniformly in an explosive mixture. Any variation of composition of the mixture (or its pressure) will cause an acceleration (positive or negative) of the wave front, and this will send a pulse out with the speed of sound which will reflect off the end wall and come back again. The departure of the compression wave will leave a rarefaction trough behind it in which the flame front will travel more slowly till the pressure is raised by the return of the pressure wave, when it will speed up again, and so on.

The combustion space will thus, from the action of a perfectly general physical law, be set into pressure oscillations at a frequency depending on the speed of the flame and of sound at that temperature, and pressure nodes will be set up, causing a series of stationary waves of pressure.

Whether the disturbance set up increases; *i.e.*, whether a sustained oscillation and a vibratory flame occurs depends on the "damping" conditions, and, for example, a flat back wall is far more likely to cause a return wave than the wedge-shaped crack characteristic of the back of a Ricardo combustion space, other things equal. A charge which is compressed enough and hot enough to pink is in a highly unstable condition (see Maxwell and Wheeler's

photos of flame acceleration) and should set up vibratory flames unless the damping conditions are extreme (*e.g.*, the wire gauze diaphragm and, of course, the Davy lamp effect in gas explosions.).

Bone's studies of flame and combustion showed that the ordinary combustion of a paraffin hydrocarbon with plenty of oxygen consisted probably in the progressive oxidation to aldehydes and ketones—thence finally to carbon dioxide, carbon monoxide and water without any free carbon formation and a colourless flame.

If before the chain indicated above has had time to complete itself the hydrocarbon is rushed through to an extremely high temperature (for example, by a detonation wave causing an adiabatic temperature rise), the instability of the hydrocarbon may be such that it cracks, giving carbon, hydrogen, and double- and triple-bonded unsaturated hydrocarbons before it has time to burn normally.

The gaseous products of the cracking will have time to burn before the wave moves on; but the carbon residues are probably in a state of aggregation, and although they will incandesce and perhaps partially burn in the crest of the pressure wave, they will be cooled in the following trough of rarefaction below the point necessary for their completed combustion.

The observation by Maxwell and Wheeler of a flash of light behind the flame front at a pink, and the fact that free carbon is always detectable in a pinked exhaust, both seem to point strongly to the existence of a " square " fronted wave emanating from the centre of disturbance, which instead of letting the flame complete itself in the quiet, hydroxylation way (Bone) cracks the partially burnt products by the sudden intense heat due to compression forming more quickly combustible products such as hydrogen, acetylene, etc., which, while they burn, incandesce the carbon residues left after they are split off.

It is therefore suggested that the method of generation of a pink is that the flame builds up into a vibrating flame and advances in a series of short rushes on the peaks of successive stationary waves while the pressure steadily rises until at one of the peaks the pressure and temperature pass over the self-ignition limit. The flame will then accelerate to, and travel at, the speed of sound at the temperature. The sudden violent increase of pressure at that point will put out a pressure wave in all directions travelling with the speed of sound which will ignite all the remainder of the charge as it travels forward and cause the flash of light behind the flame as indicated above. If the damping is such that the series of waves cannot be set up, the flame will progress steadily while the gas in front may auto-ignite as the pressure rises. In this case, as there is no surge of pressure and the pressure tapers from the flame

front forwards, there is no great likelihood of volume detonation and the flame should travel forward with a steady acceleration.

The Square Fronted Pulse.—It may at first seem a surprising claim that the volume detonation of a small quantity of the gas can put out a wave containing such a quantity of energy that it can incandesce carbon or ignite a charge; but it must be remembered that the pressure energy must flow outwards in the form of a wave, and it is the suddenness of its production that counts for most. How shattering such pressure waves can be is well instanced by the snapping of a hacksaw blade. (It is practically impossible to snap a hacksaw blade in two parts only if it is freely supported, as the rarefaction wave from the primary break reflected from the ends reinforces the tension stress in the bent parts and causes two, three or more, fractures.)

The high metallic note of the pink is due to the fact that this single pulse is arrested by the walls, and as it is a single pulse it cannot set the walls into a forced vibration in any particular frequency but leaves them to oscillate at their own natural frequency.

Some experiments were carried out by Maxwell and Wheeler to test the oft-repeated statement that an increase of pressure increased the rate of propagation of a flame, and the results certainly disproved the statement as it stands; but the statement made here (that an adiabatic increase at the flame front speeds up the flame) is not affected by these results as the conditions are totally different.

The considerations supporting the statement are as follows: The curve connecting the reaction velocity of oxidation of a hydrocarbon with temperature is as shown below.

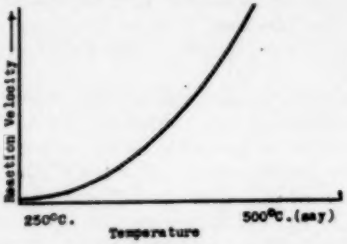


FIG. 1.

Any small portion starting at a given temperature will pass through its whole burning cycle after a time governed only by the rate of temperature rise and the reaction velocity at each increment of temperature.

A second curve can be constructed showing the general effect of the beginning temperature on the time of reaction which will

have the general shape of the following, which is the integrated reciprocal of the former curve.

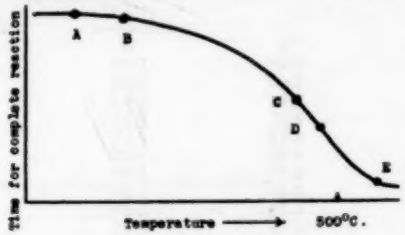


FIG. 2.

Maxwell and Wheeler's results apply to the early part of the curve near A B as they examined the effect of an increment of pressure and temperature equivalent to 15 lbs. gauge pressure adiabatic compression; the point with which flame compressions are concerned are near C D. Here it will be seen that a small increase of temperature shortens the time taken to complete the reaction greatly; and hence, since the velocity of the flame equals the fraction breadth of flame-time of reaction, speeds up the flame. As this is the case, Maxwell and Wheeler's observations are not incompatible with the acceleration postulate as at first sight they seemed to be. From about point E the curve's ordinates are a measure of the reciprocal of the velocity of sound in a gas at the temperature.

The writer acknowledges his indebtedness for facts to the authorities quoted in the text, apologising for any accidental omissions.

APPENDIX A.

In all the following A is the measured engine test, B is the ratio of the engine test of each mixture to that of the pure pro-knock, and C is the calculated engine test from the applicable formula. Volume concentrations are employed, which introduces an element of approximation, since equation (1) is based on gram-molecules; but this is so small an adjustment that it can be neglected. (It is less than the engine test permissible error.)

No. 1.

Benzene and Light Benzine Adjusted for Aromatics.

Per cent.	Diluent.	H.U.C. A	H.U.C. A^1	Ratio. B	(1+y) by calculation. C
0	—	—	4·57	1·00	1·00
10	9·0	4·7	4·71	1·03	1·03
20	18·1	4·85	4·89	1·07	1·07
30	27·2	5·01	5·06	1·11	1·11
40	36·3	5·20	5·29	1·16	1·17
50	45·4	5·43	5·57	1·22	1·23
60	54·5	5·73	5·98	1·31	1·31
	63·6	6·24			

Notes.—A^1 is obtained from A by replot, using the second column of figures, which assume 9 per cent. aromatics in light benzine. The formula from which C is calculated is $(1 + y)^{n-1} - 1 = K \log \frac{1}{1-x}$ in which K = 0·092, n = 1·3.

No. 2.

Benzene and Heptane.

Per cent. diluent.	A	(1+y) measured. B	(1+y) calculated. C
0	3·53	1·00	1·00
10	3·64	1·03	1·03
20	3·75	1·06	1·07
30	3·92	1·11	1·11
40	4·13	1·17	1·17
50	4·34	1·23	1·23
60	4·77	1·35	1·31
70	5·40	1·53	1·42
80	6·36	1·80	1·59
90	9·78	2·77	1·90

Notes.—The formula from which the figures in column C are calculated is

$$(1+y)^{n-1} = K \log \frac{1}{1-x} \text{ where } K = 0{\cdot}092.\ n = 1{\cdot}3$$

In the last column it will have been noticed that the calculated column falls off badly from the measured figures above 60 per cent. diluent. An attempt at explanation of this will be found in Appendix C.

No. 3.

Benzene and Pennsylvania Motor Spirit Adjusted to 10 per cent. Equivalent Aromatics. (Michigan).

Per cent.	Dilution.	A	A^1	B	C
0	—	—	3·98	1·00	1·00
10	10	4·10	4·10	1·03	1·03
20	19	4·21	4·23	1·06	1·07
30	28	4·34	4·37	1·10	1·11
40	37	4·48	4·56	1·15	1·17
50	46	4·73	4·87	1·22	1·23
60	55	5·08	5·35	1·34	1·31
70	64	5·65	6·14	1·54	1·42
80	73	6·46	7·63	1·92	1·59
90	82	8·13	12·35	3·20	1·90
	91	12·85			

No. 4.

Ether and Ethyl Alcohol. (*Ricardo.*)

Per cent. dilution.	A	B	C
0	2·86	1·00	1·00
10	—	—	—
20	—	—	—
22	3·82	1·34	1·34
30	4·22	1·48	1·51
40	5·01	1·75	1·77
50	6·10	2·14	2·14

Both Nos. 3 and 4 are worked from the expression

$$(1+y)^{n-1} - 1 = K \log \frac{1}{1-x}.$$

K = 0·092 for benzene and Pennsylvania spirit. K = 0·368 for ether and alcohol. n = 1·3. for both.

The figures A^1 are derived from columns 2 and 3 by replot. Extrapolating for 0 per cent. aromatics gives 3·98.

No. 5.

Mexican Spirit and Pure Anhydrous Alcohol.

Per cent. dilution.	A	B	C
0	4·45	1·00	1·00
10	4·90	1·10	1·10
20	5·30	1·19	1·20
30	5·90	1·33	1·33
40	6·60	1·48	1·48

The figures are calculated from the expression

$$(1 + y)^{n-1} - 1 = K \log \frac{1}{1 - x}.$$

$K = 0{\cdot}246$. $n = 1{\cdot}3$.

No. 6.

Benzene and Kerosine.

Per cent. dilution.	A	B	C
0	2·58	1·00	1·00
10	2·76	1·07	1·07
20	3·00	1·16	1·16
30	3·30	1·28	1·26
40	3·67	1·42	1·38
50	4·10	1·58	1·54
60	4·67	1·81	1·75
70	5·36	2·08	2·05
80	6·45	2·50	2·53

$(1 + y)^{n-1} - 1 = K \log \frac{1}{1 - x}$. $K = 0{\cdot}197$. $n = 1{\cdot}3$.

No. 7.

Iso-octane and Heptane.

Per cent. dilution.	A	B	C
0	3·53	1·00	1·00
10	3·64	1·03	1·03
20	3·78	1·07	1·07
30	3·92	1·11	1·12
40	4·13	1·17	1·17
50	4·34	1·23	1·23
60	4·62	1·31	1·31
70	5·01	1·42	1·40
80	5·44	1·54	1·54
90	6·11	1·73	1·73
100	7·42	2·10	2·10

$(1 + y)^{n-1} - 1 = K \log \frac{1}{1 - mx}$. $m = 0{\cdot}9$. $K = 0{\cdot}108$. $n = 1{\cdot}3$.

These two are good examples of the logarithmic expression, but it will be noticed that the second is a practically perfect match right up.

No. 8.

A Special Racing Mixture and Light Benzine.

L.B.	Racing M.	A	B	C
100	0	4·70	1·00	1·00
80	20	4·97	1·06	1·06
60	40	5·27	1·12	1·12
40	60	5·57	1·19	1·19
20	80	5·92	1·26	1·26
0	100	6·32	1·34	1·34

$(1 + y)n^{-1} - 1 = K \log \frac{1}{1 - mx}$, where K = 0·413, m = 0·2, and n = 1·3.

It has been more convenient so far to work with the engine test ratio, but it can be seen with a little consideration that as the denominator of the ratio is the (constant) engine test of neat pro-knock, the logarithmic consideration is also correct if the improvement in engine test is stated as an engine ratio (C.R.)

This will be accordingly done after the next two examples, tetralin and decalin.

No. 9.

Tetralin (Tetrahydronaphthaline).

Per cent. dilution.	A	B	C
0	4·7	1·00	1·00
10	4·9	1·04	1·04
20	5·1	1·08	1·08
30	5·3	1·13	1·13
40	5·5	1·17	1·17
50	5·7	1·21	1·21

$y = k.x$, where $k = 0·42$.

The actual error in taking $(n-1)y$ for $(1+y)^{n-1}-1$ at these ratios is only 3 per cent. at 1·20 and 0·3 per cent. at 1·16, and in the remaining examples the ratio is well below this, as the engine had a zero on pro-knock of about 6·3 : 1.

No. 10.

Decalin (Decahydronaphthaline).

Per cent. dilution.	A	B	C
0	6·3	1·00	1·00
10	6·17	0·98	0·98
20	6·05	0·96	0·96
30	5·92	0·94	0·94
40	5·80	0·92	0·92

$y = k.x$, where $k = 0·2$

No. 11.

Cyclohexene.

Per cent. dilution.	Engine test increase with per cent. dilution.	Estimate.	Per cent. dilution.	Engine test increase with per cent. dilution.	Estimate.
0	0·00	0·00	60	0·98	0·99
10	0·25	0·26	70	1·01	1·00
20	0·45	0·49	80	0·98	0·98
30	0·65	0·68	90	0·90	0·90
40	0·78	0·82	100	0·80	0·80
50	0·88	0·92			

The estimates are made from $y = ax - bx^2$; where $a = 2·86$, $b = 2·06$.

No. 12.

Tetramethylethylene.

Per cent. dilution.	y	Calculated y (a=7·82, b=15·3).	Per cent. dilution.	y	Calculated y (a=7·82, b=15·3).
0	0·0	0·00	15	0·8	0·8
10	0·6	0·63	25	0·95	0·95

$(y=ax-bx^2)$

No. 13.

Cracked Spirit, 200° End Point.

Per cent. dilution.	y	Calculated y (a=1·05, b=0·22).	Per cent. dilution.	y	Calculated y (a=1·05, b=0·22).
0	0·00	0·00	50	0·47	0·47
10	0·11	0·10	75	0·64	0·64
25	0·25	0·25	100	0·83	0·83

$y=(ax-bx^2)$

No. 14.

Cracked Spirit, 175° End Point.

Per cent. dilution.	y	Calculated y (a=1·49, b=0·38).	Per cent. dilution.	y	Calculated y (a=1·49, b=0·38).
0	0·00	0·00	50	0·65	0·65
10	0·16	0·15	75	0·88	0·91
25	0·37	0·35	100	1·11	1·11

$y=(ax-bx^2)$

No. 15.

Cracked Spirit, 150° End Point.

Per cent. dilution.	y	Calculated y (a=2·33, b=0·78).	Per cent. dilution.	y	Calculated y (a=2·33, b=0·78).
0	0·00	0·00	50	0·94	0·97
10	0·24	0·22	75	1·30	1·31
25	0·53	0·53	100	1·55	1·55

$y=(ax-bx^2)$

APPENDIX B.

Let the rate of reaction of proknock and the absolute temperature be connected by some such relation as Fig. 1 (p. 9):

$$\frac{dR}{dt} = K.\ f(\theta).$$

The rate of heat release varies with the rate of reaction, and since in the case of a mixture the diluent is assumed to produce no heat:

$$\frac{dH}{dt} = K_2 q \left(\frac{dR}{dt}\right) = K_3\ q.\ f(\theta).$$

But

$$\frac{dH}{dt} = C_v \frac{d\theta}{dt} = K_3\ q.\ f(\theta).$$

And, re-arranging and integrating:

$$qt = \frac{K_3}{C_v} \int \frac{1}{f(\theta)}\, d\theta + C.$$

Or, from the given temperature θ, and to the constant S.I.T. θ_2, $qr = C_2$.

APPENDIX C.

In endeavouring to explain why the benzene-heptane curve breaks away at 60 per cent. the writer expresses in the paper the view that benzene begins to act as oxygen stealer at the compression temperatures reached.

In an attempt to survey the possible effect some figures, due to Mr. Fenning (Appendix 1, Aero Res. Com. R. & M., 979), were employed.

These figures deal with the action of benzene and hexane respectively on air at precombustion temperatures, and as they are of considerable interest the writer reproduces them here in full.

Reaction of Benzene and Air at Medium Temperatures.

(Fenning.)

Approx. temperature at which charge was sampled.	Approx. time from start of baking in vessel.	Percentage by volume of CO_2.	Corresponding rate of reaction.	Rate of reaction calculated from Van't Hoff's Isochore.
227° C.	1 hr. 10 mins.	0·12	1·7	1·7*
252° C.	1 hr. 40 mins.	0·24	4·0	5·39
278° C.	2 hrs. 15 mins.	0·74	14·3	14·3
304° C.	3 hrs.	2·39	36·8	36·3
323° C.	3 hrs. 30 mins.	5·98	119·7	76·7

* Theoretically, reaction starts at 202° C.

Reaction Between Hexane and Air at Medium Temperatures.

(Fenning.)

Approx. temperature at which sample was taken.	Approx. time from start of baking in vessel.	Percentage of CO_2 in sample.	Corresponding rate of reaction.
201° C.	10 mins.	0·02	—
226° C.	54 mins.	0·04	0·74
256° C.	1 hr. 30 mins.	2·04	55·5
278° C.	2 hrs. 1 min.	3·56	49·0
303° C.	2 hrs. 40 mins.	5·79	57·0

Above 230° C. the reaction is quite unstable—several explosions took place.

If the rough assumption is made that the average reaction temperature of the benzene is that of the final compression temperature (a) (owing to the "dwell" of the piston at T.D.C. there is something to be urged for this), it is possible to calculate a corection figure based on the reaction rate at that temperature; which, when added to the theoretical log figure, gives the practical figure up to 80 per cent. dilution. Above this (at the extremely high compression ratios) it is so very difficult to measure H.U.C.R.'s with any degree of accuracy that the practical figures themselves are doubtful, and attempts to match them would be of no value whatsoever.

Heptane/Benzene.

Correction for Activity of Benzene Above 200° C.

Percentage Diluent.	H.U.C.R.	Compression Temp.	Rate of reaction of benzene (Van't Hoff figures).	Theoretical improvement of H.U.C.R. (1 + Y).	Add improvement due to oxygen seeking of benzene.	Total theoretical improvement.	Practical from Col. 2.
0	3·53	200° C.	0	1·00	0	1·00	1·00
10	3·64	204° C.	0·25	1·03	0·002	1·03	1·03
20	3·75	209° C.	0·49	1·07	0·0049	1·07	1·06
30	3·92	215° C.	0·74	1·11	0·0074	1·12	1·11
40	4·13	223° C.	1·4	1·17	0·014	1·18	1·17
50	4·34	230° C.	2·1	1·23	0·021	1·25	1·23
60	4·77	245° C.	4·4	1·31	0·044	1·35	1·35
70	5·40	265° C.	9·0	1·42	0·090	1·51	1·53
80	6·36	291° C.	23·1	1·59	0·231	1·82	1·80
90	9·78	369° C.	*	1·90	—	—	2·77

* Benzol breaks away rapidly above 300° C.

NOTES.—Column 3 assumes an initial temperature of 50° C. Column 4 is calculated on Fennings results. Column 5 + column 6 = column 7. Column 6 = column 4×10^{-2}.

DISCUSSION.

The President said that it was interesting to find a new line of research or investigation opened up on this difficult subject of detonation. Personally he was not going to attempt any criticism of the paper, but only to raise two quite minor points.

The author had mentioned that the value of knock was largely æsthetic. That might be so in the stages of initial knock, but surely in the case of aeroplane engines, if the knock was intense, the results might be the very reverse of æsthetic.

His second question was with regard to compression ignition in a dirty, spark-ignited engine. He doubted whether that could be really compression ignition.

Dr. E. Mardles (of the Air Ministry Laboratory, Imperial College of Science) said that he had listened with great interest to the paper, which was certainly a very interesting and praiseworthy effort to deal mathematically with a complex problem. Undoubtedly it would help to clarify their ideas and to dispose of erroneous ideas and hypotheses, or, at least, to set limits to their

speculations. He thought that the author had struck a very happy note early in his paper when he referred to the nuclear hypothesis of the late Prof. Dixon. Many scientists, especially physicists—Kelvin and Maxwell, for instance—had dwelt on the significance of nuclei. Lord Rayleigh, working on the phosphorescent glow, found that water vapour and camphor vapour inhibited the phosphorescent glow of phosphorus vapour, and ascribed it to the fact that nuclei were in some way rendered harmless. A similar explanation was given by Dixon with regard to the effect of inhibitors, such as ethylene, on the phosphorescent glow of carbon disulphide vapour in air. Then they had the late Prof. Callendar's work as a physicist. In 1924 Callendar put forward the hypothesis that the large influence that compression had on detonation was in some way connected with the cloudy condensation of nuclear particles in the fuel charge during compression. His ideas had been published on the matter, and later, when the chemical side of the work was investigated, it was found that the fuel vapours were peroxidised—that is to say, these active nuclei were not only kinetically, but also chemically, activated.

More recently these ideas of the function of nuclei in gaseous systems had been developed, and now one spoke of the active centres from which originated chain reactions. The active molecules were capable of activating their neighbouring molecules, which in their turn activated their neighbours, and so, as it were, from each centre there were chains of reactions passing out. When the number of active centres formed per unit time was greater than the number of those broken, then the gaseous reaction got out of hand and self-ignition and explosion set in.

Referring to the first assumption of the author with regard to the quantity of the catalyst or "irritant"—he had expressed it according to the simple dilution law—he thought that some years ago Mr. Ricardo and Mr. Alcock found this effect with diluents such as cooled exhaust gases on detonation. In an internal combustion engine they found that hydrogen, nitrogen and carbon dioxide behaved as true diluents, but steam was found to behave in a manner more than a diluent. Had the author considered that gaseous fuel vapour in excess could act as a diluent?—for this reason, that the onset of detonation in an engine was very sensitive to mixture strength. For example, if the mixture strengths were plotted as the abscissæ and the detonation tendency as the ordinate, there was a particular mixture strength where there was maximum detonation. He had studied the action of mixture strength on the yield of peroxides of hexane, and had found that the peroxidation and the tendency to detonate could be closely correlated. Maximum knocking and the maximum peroxidation occurred at a mixture

strength of about 7 per cent. hexane in air. It could be considered that below this particular point there was excess oxygen, and, on the other hand, above it there was excess fuel vapour. It would be of interest if the author could deal with this problem mathematically, because with the lean mixtures oxygen could be considered as a diluent—and it appeared quite certain that oxygen did behave as a diluent—and, on the other hand, with excess fuel vapour the fuel vapour might be regarded as a diluent.

There was another factor which came in, and which, he thought, had not been emphasised by Mr. Duff. The reaction for peroxidation could be expressed by the chemical equation—

$$F+O_2=F[O_2]^*$$

where F stood for the fuel molecule, the star indicating activation and $F[O_2]^*$ the irritant of which Mr. Duff had spoken. In the original paper, of which he (the speaker) was one of the authors, it was assumed that the organic peroxides primarily formed were alkyl hydrogen peroxides, but they had never isolated them. Recently, in France, chemists had reported the isolation and identification of these organic peroxides.

Another important equation followed from the first, because it was found that the peroxides were attacked by the fuel vapours themselves, the active peroxide being destroyed and producing inert combustion products. The peroxides were thus destroyed by their own excess fuel vapours. From the first equation the proportion of hexane to give maximum peroxidation should be about 33 per cent., and as a matter of fact it was only about 7 per cent. In other words, the combustion was mainly an autoxidation process, according the the equation—

$$F[O_2]^*+F=2\,FO$$

where FO represented inert oxidation products.

What he wanted to point out in addition was that in the second equation the fuel vapour, F, might be replaced by a molecule of an anti-knock. If benzene was added to the petrol mixture undergoing combustion, one found that the peroxide of the fuel vapour attacked the benzene, producing phenol, etc., as in the equation—

$$F[O_2]^*+C_6H_6=C_6H_5OH+FO.$$

The author had stated that benzene acted as a diluent, but it did more than that, it attacked the peroxides, as did ethylene. The result was to form ethylene oxide.

$$F[O_2]^*+C_2H_4=C_2H_4O+FO$$

In a paper just presented to the American Chemical Society, Lenhir had found that one of the primary reactions in the oxidation of ethylene was ethylene oxide, and the speaker considered this to be a comfirmation of the view that ethylene was oxidised by its own peroxide. Benzene, ethylene and most fuel vapours attacked

the peroxide, so that one could not speak of them as simple diluents. The dilution factor did come into the problem, but in addition one must consider the other factor, namely, the active oxygen-using capacities of the substance. He imagined that it would be possible to get a general equation covering both effects.

There was just one other point which might be of interest. The author had mentioned the induction period, to which recently a good deal of attention had been paid in this and other countries. Brunner had found that if a gas mixture were placed in a bulb under isothermal conditions the peroxide or active oxygen could be estimated from time to time, and it was discovered that peroxidation was at first slow, then very rapid, after which explosion occurred. If one correlated the amount of active oxygen formed with the rise of pressure and the rise of temperature, there appeared to be a very close relationship, as the author had assumed. If one measured the temperature rise in a system, at first there was a fall in temperature and then a rapid rise, corresponding to the point where the peroxides accumulated and "popped off." The initial fall in temperature was presumably due to the fact that the formation of peroxides was endothermic—that is to say, they were taking energy out of the system so as to form these active centres. Then if one measured the pressure rise with time one found a similar kind of thing—a fall at first, then a rise, and afterwards steadiness. He thought that this behaviour fitted in with the author's assumptions very well.

There was one interesting point which arose out of what the author had said with regard to the lag or wait period and the temperature coefficient of reaction. The rates of reaction when the time of heating was just a few seconds had been recently worked out and published for a large number of fuel vapours at different temperatures. For a pro-knock substance, like normal hexane or ether, a very steep curve relating temperature and reaction rate was obtained. At a temperature of about 276° there was a sudden rise in the rate of reaction, although at first the reaction with rise of temperature was very slow. The slope of the curve indicated the temperature coefficient. If an anti-knock substance like ethylene were taken, however, quite a different behaviour was noticed. Here the curve showed a much less marked slope, indicating that the temperature coefficient of the gaseous reaction of ethylene in air was much lower than that of the pro-knock substances. Taking benzene and toluene as other interesting cases, these oxidise at much higher temperatures, and the temperature coefficient of oxidation for toluene was much less than for benzene, which was not so effective as toluene in delaying detonation. The self-ignition temperature, therefore, was not so important a factor as the temperature

co-efficient of the gaseous reaction. Tizard and Pye, from their investigations, had pointed out that the temperature coefficient of gaseous reaction was of main importance in this question of knocking, and he (the speaker) had examined scores of fuel vapours and had found their conclusion borne out by later work. The pro-knock fuels had a very high temperature coefficient, whilst the anti-knocks had a very low temperature coefficient, and that could be explained in terms of the peroxide theory.

The first equation of peroxidation which he had given, namely—

$$F+O_2=F[O_2]$$

was important with the pro-knock substances, whilst the second equation of autoxidation was important with ethylene, benzene and toluene, etc. When the vapours of these substances tended to react with their own peroxides, one got inert substances, and therefore a much lower rate of reaction at higher temperatures. It would be interesting to know whether the author could deal with that point, using the two equations. The facts had been published and were quite favourable for mathematical analysis.

Mr. R. Stansfield said that while the analyses given by the author explained the particular cases stated in terms of certain assumptions, there were several types of fuel behaviour met with in practice which seemed to need additional assumptions, or possibly, as Dr. Mardles had just suggested, a general equation which would meet all the facts. He would like to ask Mr. Duff when he dealt with the effect of mixture strength on knock to include, if possible, an explanation of why the increase of H.U.C. was very marked for a given decrease of mixture strength, and not nearly so marked for an equivalent increase of mixture strength. The fall in knocking was very marked to the weak side and not nearly so marked to the strong side. A further example which seemed to need other factors than those given for its explanation was that of temperature effect on ternary blends. When a paraffin was compared with octane/heptane in certain engines, and also with blends of paraffin and pure benzene, it was found that the octane values determined for any blend were only very little lower at high jacket temperatures than at low. The change between a 50° C. jacket temperature and one of 170° was only of the order of one to two octane numbers. The change was greatest for the blend with the highest concentration of benzene, but in practice it was quite unimportant. If tetraethyl lead were added to the unblended paraffin, or the benzene blends with the paraffin, there was still no marked temperature effect. If one explored the whole range of lead sensitivity as the temperature rose it was found that the sensitivity might first fall and then rise slightly again. When a naphthenic base was substituted for the paraffin, the octane

rating fell considerably with rise of the jacket temperature. The fall might be several octane numbers. If lead was added in a certain proportion to the naphthene-benzene blend, or to the naphthene alone, the reverse effect was obtained, the octane value of the ternary blend with lead increasing out of all proportion, and it might be much higher for such a ternary blend at high temperatures than for a paraffin-benzene-lead blend which matched at a low temperature.

An important practical point was mentioned in the author's comments on the results from different engines. It was generally known that two engines of different makes might give different octane ratings. It had also been found, although it had not been emphasised, that a new engine might give similar differences from an older one of the same make. This observation is not from an isolated case. The speaker knew of four cases, and was examining a possible fifth, which showed this behaviour. It was also found that a further change in relative rating was liable to occur just at the end of the useful life of the engine cylinder. These results had been traced to the effect on conductivity of initial deposits of rust in the water jacket, and to changes which took place towards the end of engine life when the piston rings and cylinder were affected to such an extent that complete sealing was not obtained at the end of compression. He was bringing forward these facts because he felt that the author might have over-emphasised fuel characteristics, even to the extent of introducing non-existent effects, and not have ascribed enough to the engines themselves. While every effort was made to control engine variables, there were many variables which were badly uncontrolled.

With regard to the break away of the actual from the theoretically derived log curve for case 1, possibly the uncontrolled variables of any method of engine test might be a sufficient explanation. As compression ratio was increased, the exhaust valve temperature, the residual diluents, and several other factors altered, and it seemed probable that the rate of alteration became rapidly more important at just those higher ratios which were necessary to make a 50 to 60 benzene blend knock. In view of Mr. Duff's further corrections he supposed that the critical point must be raised to the region of an 80 per cent. blend.

Mr. I. A. J. Duff, in reply to the President, said that his remark that knock had very little practical significance was intended to refer to the type of knocking one heard on the road, which was what he had in mind. Of course, when one was stressing the engine right up to the limit, as in an aero engine, it was rather a serious matter, and besides this, one was getting near the point where pre-ignitions were important.

With regard to compression ignition in a dirty engine, a really dirty engine had got its cylinder more or less coated with a poor conductor, and it was just possible that although there might be a red hot point to set the charge off, the ignition might be due to the fact that the heat had been kept in more efficiently by lack of loss of heat to the walls. He would not, however, put the red hot point out of court.

In reply to Dr. Mardles, many of the points he brought out on the board had been unknown to the speaker, and they would give him a great deal of food for thought. But he (the speaker) got at the same sort of result by looking at things in rather a different way. Dr. Mardles had shown that there was a deoxidising effect of the peroxides by further action of the fuel. He was not aware of that, but he had looked at the matters as follows: Supposing one had 100 oxygens, and 10 of these were active, he had assumed that the pro-knock got two and the anti-knock kept off the other eight simply by obstruction. Dr. Mardles had shown that the pro-knock might get all ten and the anti-knock then proceeded to steal eight of them. In practical politics the results might be the same, but, of course, Dr. Mardles supplied an explanation of part of the chain. The contents of Appendix C were undoubtedly strengthened by what Dr. Mardles had said. The point Dr. Mardles had mentioned about ethylene diluents and about having the best mixture seemed to go rather with the point which Mr. Stansfield had raised later, that one got a large decrease of H.U.C. on the "lean" side and a small one on the "fat" side. Supposing it was a case of a fuel merely acting as a diluent, if one had to get 100 molecules into a given space, and 60 of those were oxygen and 40 were fuel, if ten more fuel were inserted it would mean that one would get ten less oxygen in, and the proportion of "active" oxygen, and hence of peroxides, would be lowered, *i.e.*, the fuel would act as diluent.

He thought the point which Mr. Stansfield had raised about the decrease of H.U.C. was only to be explained by the fact that on the weak side there was less fuel to be attacked and on the strong side more fuel to be attacked, but at the same time it was keeping oxygen out.

He would like to thank Dr. Mardles for a verbal contribution well calculated to fill up with experimental facts certain places where he had had to assume and guess.

Replying to Mr. Stansfield, he regretted that ternary blends did not as yet lend themselves to study under the theory owing to lack of data, and so in his own paper he had confined himself to blends of two. Probably what Mr. Stansfield had said about the

curious behaviour of ternary blends might be due to the competition for oxygen of the various components, but the question could only be approached by careful collation of figures.

The other point Mr. Stansfield had raised was about different engines having different reactions to the same mixture. Supposing one had two mixtures, A and B; one engine would place A above B, and the other place B above A. That was a very difficult problem, but he did not think it arose in the binary blends, which were all that he had attempted to deal with, as the evidence went to prove that it was due to a temperature effect involved in the effects with complicated mixture. He was not quite sure, but he thought that a curious behaviour was observed with certain fuels, a wobble effect, whereby they started off with a very little drop, then rose again, and he would not like to say that something of this kind did not enter into the action.

A vote of thanks was accorded to the author, and the meeting terminated.

The following written contributions to the discussion were subsequently received.

From Mr. E. C. Craven:

The author is to be congratulated on the ingenious manner in which he has arrived at the form of the composition H.U.C.R. curve for fuel mixtures. In a qualitative way also there is little doubt that many of the fundamental assumptions made are in fact major factors in the pre-detonation actions.

The fact, however, that the function derived appears to fit the experimental results reasonably well can hardly be taken as very convincing proof of the whole of the theory propounded by the author. Many of the steps in the deduction can be greatly modified without in the least influencing the degree of accuracy with which the final function would fit the experimental figures. From the mere standpoint of finding a function to fit the observed curves it would be easy to guess many forms equally good.

In the author's initial equation, viz.—

$$q=(1-x)$$

x appears to be the weight fraction of one of the constituents of the mixture. Since the oxidation reaction will more probably be proportional to the partial vapour pressure of the constituents in the mixture, x and $(1-x)$ should be molecular fractions. The introduction of the active oxygen hypothesis seems quite unnecessary. On the large scale acetic acid is prepared by the oxidation of aldehyde through the intermediate stage of acetyl peroxide, the bulk of the oxygen being consumed. It would be ridiculous to suppose that all this oxygen was in an active form. Moreover, as in the internal combustion engine there is no radiation present

of sufficiently high quantum to activate oxygen. It is much more likely that, as suggested by Ormandy in connection with spontaneous ignition temperatures, the more cumbrous fuel molecules are the bodies activated, it being known that these absorb strongly those radiations emitted most strongly by a "black body" at temperatures of the same order as the ignition temperatures found. In any case whatever may be the intermediate mechanism it is only necessary to assume some ordinary reaction between the fuel and oxygen molecules, the first equation will still hold.

In connection with the subject of peroxides, strong objection must be taken to the statement that these were discovered by Callendar and his co-workers. Moreover, high temperatures are not necessary for their formation, indeed, with aldehydes and olefines greater concentrations may be obtained at low temperatures, since then the further reaction between peroxide and the aldehyde or olefine is diminished.

In equation (10) it will be noted that there are two constants which may be adjusted to fit the experimental curves. This really means that the formula is made to fit the observations at *three* points. It would be far more satisfactory proof of the author's view if the quantity m expressing the relative peroxidisability of the two constituents could be confirmed by experiments apart from the test engine. In general, also, it should be possible to give some meaning to the constant K which figures so largely.

The ignition temperature β taken by the author seems to be an initial flame temperature. This must, on the author's theory, be capable of being expressed as a function of the S.I.T. as ordinarily determined. If the constant K could be determined by considerations of this nature and m by separate experiment, then there would be a basis on which to test the theory. As it is there are too many arbitrary terms.

From **Dr. G. B. Maxwell:**

As Mr. Duff made clear in his paper, the "self-ignition" theory of pinking is no new thing and its failure to receive general acceptance has been due to its inability to explain certain experimental facts. The close agreement in his paper between observed facts and calculations based on the assumptions of the theory must therefore lead to very careful scrutiny of the mathematical treatment. Such a scrutiny leads to the conclusion that there is an error in the development which vitiates the results.

Equation (6)— $$q\tau = C_2$$

where τ is the "wait time" elapsing, at critical knock, between the commencement of "irritant" formation in a small, but fixed,

amount of unburnt charge and the moment when the ignition temperature is attained in this small residue.

This relationship is derived in Appendix B, p. 11, in which τ is the time required for a pro-knock air mixture to self-heat through the same temperature range entirely by its own internal reaction. The τ derived in this manner is not applicable to the case of critical knock, and an inspection of Appendix B shows where the difference lies. It is there stated that, in the case of the self-heating pro-knock, "the rate of heat release varies with the rate of reaction," thus—

$$\frac{dH}{dt} = C_v \frac{d\theta}{dt} = K_2 q \left(\frac{dR}{dt}\right)$$

In the case of the residual charge in an engine $\frac{dH}{dt}$ is determined not only by the rate of reaction but also by the heat of compression, thus—

$$\frac{dH}{dt} = C_v \frac{d\theta}{dt} = K_2 q \left(\frac{dR}{dt}\right)$$

It is quite plausible to asume that the reaction time of the "irritants" in an engine at critical knock is some function of q, but the relationship is obviously not given by equation (6).

From **Mr. Evelyn S. L. Beale :**

There is a considerable amount of experimental evidence in favour of the self-ignition theory of pinking, and a mathematical development, based on the assumptions of the theory, which led to conclusions in agreement with experimental facts, would give further support to the theory.

The co-ordination of this theory with the law of mass action, applied to the concentration of oxygen and pro-knock as is attempted by Mr. Duff seems to be a very promising line of attack.

Unfortunately, in this paper the derivation of equations (5) and (6), upon which the whole structure rests, does not appear to be at all satisfactory, as is shown by the following examination based on the fundamental assumptions given in the paper.

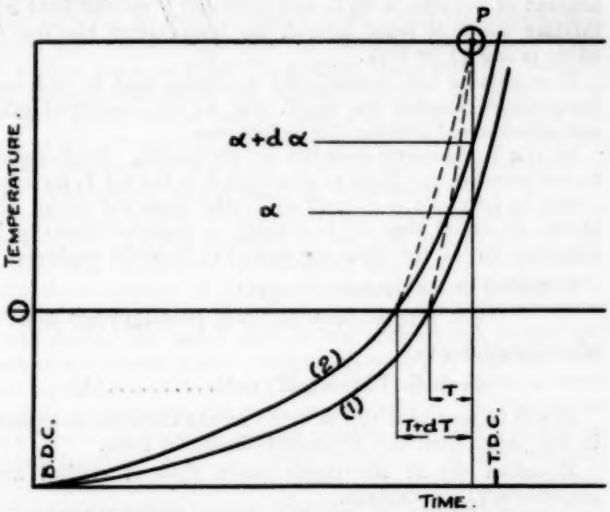
These are that :—

1. Some of the unburnt charge detonates as soon as it reaches its Self Ignition Temperature, a constant temperature independent of q.

2. Above a certain lower temperature θ heat is evolved, due to the formation of irritants at a rate determined by q, and the temperature at each instant.

3. Under critical knocking conditions the combined effect of the rise of temperature due to this cause and due to compression by the piston and by the burning of the rest of the charge just brings the temperature of the remainder to the S.I.T. at a fixed point in the stroke close to Top Dead Centre.

The conditions can then be represented simply by means of a diagram, as follows :—



The two full line curves (1) and (2) represent the rise of temperature of the detonating section of the charge in two blends working at critical knocking conditions, in the absence of heating effects due to irritants.

Curve (1) represents a low compression ratio and a fuel containing a large amount of irritant, while curve (2) represents a higher compression ratio with a smaller amount of irritant. These curves are, of course, not to scale, but illustrate qualitatively the conditions in the two cases.

The point P represents the occurrence of the pink.

At a point on each curve where the temperature is equal to θ the formation of irritants begins and raises the temperature at such a rate as to reach the point P as indicated by the dotted lines.

Now if the rate of formation of irritants in pure pro-knock is a function of temperature, $f(\theta)$, the rate of formation in a mixture is $q\,f(\theta)$ and if c is the heat of reaction the rate of heat input is $cqf(\theta)$.

The heat produced in this way will depend on the actual time-temperature path by which P is reached due to all causes.

This one would expect to be an extremely complex curve, but in order to carry the discussion a stage further it might be assumed that since the temperature limits are the same in both cases, although the times are different, the average value of $f(\theta)$ will be the same in both cases and is equal to k say; therefore the total amount of reaction is kqT, and assuming a specific heat σ of the mixture which is being heated, the temperature rise due to this cause is $kc\sigma$ qT or KqT.

Now putting into symbols the condition that in each case the temperature reaches the S.I.T. due to the combined effects of compression and heating due to irritants.

let q a T represent quantity of pro-knock. Temperature due to compression, and Time to pass from θ to the S.I.T. for curve (1).

and (q+dq), (a + da), (T+dT) the same for curve (2). It should be noted that dq is actually a negative quantity in this notation, but all the signs are kept +ve to avoid confusion.

Referring to the diagram, we get

$$a + KTq = (a + da) + K\,(T + dT)\,(q+dq)$$

which simplifies to

$$da + K\,(Tdq + qdT) = 0 \ldots\ldots\ldots (A)$$

It will be seen that this is by no means the same as equation (5) in the paper, although somewhat similar in form.

Equation (6) in the paper states that at critical knocking conditions qT = constant.

It will be quite clear from the foregoing remarks that, since the temperature rise due to the formation of irritants is equal to KqT and the fundamental assumption of the theory is that at critical knocking conditions the temperature rise due to this cause varies so as to bring the final temperature to the S.I.T. in each case, the value of KqT cannot possibly be constant—it therefore appears that equation (6) is wrong.

The result of assuming KqT to be constant can readily be seen from the diagram since in this case, as the S.I.T. is assumed constant, a must be constant.

In other words, in order to maintain critical knocking conditions the compression ratio must not change.

This result is also obtained by making the substitution qT = constant in the equation (A) above which then reduces to $da = 0$.

This incidentally is a check on the validity of the equation (A) in representing the results of the initial assumptions.

Moreover, since the whole basis of the theory is that the temperature rise due to formation of irritants varies so as to compensate for the variation in a at critical knocking conditions, any equation in which the substitution $KqT = \text{const.}$ is made and which does not then give $da = 0$ must, *a priori*, be wrong.

It is noticeable that this applies to equation (5) in the paper.

Dr. V. Henny: The theory of detonation as given in the paper is in line with the generally accepted theory that the initial rapid burning of the charge compresses the still unburnt portion of the charge to that point at which the ignition temperature is reached, thereby causing this previously unburnt portion to ignite; this results in a rapid rise in temperature and pressure causing the emission of a wave pulse of extremely sudden increase in pressure, the impact of which on the walls of the cylinder and combustion chamber produces the knock, pink, or detonation.

It is interesting to note that detonation or knocking is caused by an interaction of a small quantity of the fuel and oxygen of the charge and that the increase in knocking tendency varies directly with the concentration of oxygen in the charge; furthermore, that only a small portion of the oxygen content is reactive and then only during the latter part of the compression stroke and first part of the burner period, during which time it combines with any pro-knock present forming "irritants" which cause a more or less rapid temperature rise until ignition sets in. In the case of knocking fuels, the active oxygen reacts with the pro-knocks (peroxides) forming "irritants," while in the case of non-knocking fuels, the olefins, tetraethyl lead, iron carbonyl, etc., have such great affinities for active oxygen that only a small amount, if any, is available to react with the pro-knocks present.

In other words, detonation can be reduced by reducing the amount of knock inducing "irritants." This can be done either by displacement of the pro-knocks by a non-irritant forming anti-knock such as benzole, or by dilution of the active oxygen with inert diluents such as nitrogen, or by addition of oxygen stealers such as tetraethyl lead and iron carbonyl.

This theory sounds reasonable, especially in view of the fact that almost a year ago we determined in our Riverside Laboratories the anti-knock or pro-knock value of a number of gases including CO, CO_2, N_2, H_2 and O_2; and it was noted that adding 3 per cent. of oxygen to the air in the charge increased the knock intensity as much as either 8 per cent. of nitrogen in the air or 32 per cent. of benzole in the fuel decreased the knock intensity. You will note that these findings are in line with Ricardo's results as mentioned in the paper.

A number of theories have been propounded from time to time. In our work we have not attempted to prove or disprove any existing theories or develop a new one; we have limited our work to developing a suitable knock-testing apparatus and an accurate and reproducible method for testing and rating fuels which would duplicate actual automobile performance as closely as possible. However, with the suggestion that the non-knocking characteristic of a fuel was due in some way to the formation of CO during initial burning, subsequent tests showed that 3 per cent. of oxygen added to the air in the charge increased the knock intensity as much as either 2 per cent. of CO in the air or 32 per cent. of benzole in the fuel decreased the knock intensity. It was also noted that 3 per cent. of H_2 had about the same effect as 3 per cent. of CO.

Just what the chemical action is that either induces or suppresses detonation is still a debatable question. We do know definitely, however, as a result of extensive photographic and visual flame study by T. A. Boyd, General Motors Research Laboratories, that detonation is due to a many-fold increase in the rate of inflammation within the latter portion of the charge.

Mr. I. A. J. Duff, in reply to the written contributions, writes:—

In reply to Mr. E. C. Craven, the point of view which he puts forward, that other functions may be found which will fit the results equally well is probably correct as to the last two cases, but the author is not sure that this can be sustained for the first two. The history of the derivation of the expressions has been an extended series of approximations, but each time a new correction has been made it has filled up some little gap in the theory and at the same time it has made the theoretical figures converge on the practical. The matter contained in appendix C is a good example of what the author means by this.

The paper mentioned "active" oxygen, but it was not intended to imply that this is "activated" or quantised oxygen—the writer thought of it as probably being the high speed molecular content or possibly the high speed content which happens to strike a fuel molecule in the correct attitude?

The writer was certainly under the impression that Callendar and his co-workers were the first to record the facts which are usually lumped together under the title of the "peroxide theory" and associated with their names: perhaps Mr. Craven will give him the references on which he bases his objection, as it is a point which should be cleared up.

The author agrees entirely with Mr. Craven as to his remarks regarding equation 10 et seq. He was badly hampered by a total lack of facts in his attempt to study β. A little research carried out on the points to which he draws attention would undoubtedly

be most valuable in that it would provide corroborative evidence or, if the theory does happen to be wrong, as other equally plausible theories have been in the past, would knock the bottom right out of it. Actually the matters mentioned by Dr. Mardles are closely akin to this, and future developments seem likely to come from that quarter.

In reply to Dr. G. B. Maxwell, his attack on equation 2, $q\tau = \text{const.}$ seems to be founded on a misapprehension of the writer's intentions in including Appendix B.

Appendix B. shows that if heat gains or losses be disregarded, and it be assumed that the diluent has no heating effect, $q\tau = \text{const.}$ This is obviously only an approximation to practice as heat is lost to the walls even in a self-ignition apparatus.

In the engine, on the other hand, heat is at the same time being lost to the walls by the residual charge, and being gained by it from the compression going on as a result of the combustion of the rest of the charge—and these two effects must tend to be balancing out to some greater or less extent.

Some assumption as to the connection between q and T must be made if we are to integrate equation (5), and the considerations stated above led the writer to select $q\tau = \text{const.}$ and $T = \tau$ as being suitable and likely.

It is certainly never very far from the truth, and in test engine conditions the assumption seems justified by the results.

In replying to Mr. Beale, it is necessary first to draw attention to three important inaccuracies in Mr. Beale's contribution. These are as follows :—

1. His citation of fundamental assumption (3) is not in accordance with anything said in the paper. It is nowhere stated that the residual charge arrives at its S.I.T. at a fixed point in the stroke, and, indeed, this is contrary to the author's considered belief.

2. His diagram shows α, $\alpha + d\alpha$, the compression temperatures as attained at a fixed point before T.D.C., whereas inspection of equation (2) and the lines immediately preceding would have shown him that this takes place at T.D.C.

3. He quotes the author as stating in equation (6) that at critical knocking conditions $qT = \text{const.}$

Equation (6) states that $q\tau = \text{const.}$ and three lines lower it is stated that at the critical knocking point $\tau = T$.

The writer prefers these statements kept separate and not telescoped into one, as otherwise the mechanism of the attainment of critical knocking conditions is obscured and lost.

Equation A which is obtained in the discussion by development from first principles can be obtained more simply and directly

while at the same time exhibiting the expression from which it is derived, and without making use of his diagram which is vitiated by the errors mentioned, as follows :—

Let $\alpha+KqT=\beta$ ..... A. 1.

Taking the total differential for two independent variables

$$d\alpha+K\left\{\frac{dqT}{dq}\right\}_{T}dq+K\left\{\frac{dqT}{dT}\right\}_{q}dT=0$$

which develops into

$$d\alpha+KTdq+KqdT=0.....A.$$

Now there are plenty of reasons for thinking that $q\tau=$const. is approximately true—see reply to Dr. Maxwell and Appendix B., and there is photographic evidence in favour of the assumption that $\tau=T$ so that the substitution of $qT=$const. into A.1 makes α always constant.

Now this last as he says is absurd, but this merely makes the supposition that the heating law is KqT absurd and does not have any bearing on the supposition that $q\tau=$const. or on $T=\tau$ since they depend on considerations abundantly established elsewhere.

The author regrets that by an unfortunate oversight at one point in his paper he left the expression

$$\alpha+KqT=\beta$$

uncorrected in the galleyslip. This should, of course, have read

$$\alpha+Kf(q, T,)=\beta$$

to be in consonance with the rest of the work.

He abandoned the hypothesis put forward in the earlier galleyslip that KqT represented the chemical heating in favour of the much simpler "balance" equation as a result of some discussion he had with Mr. Beale, and is therefore rather surprised to find the latter putting it forward as a workable hypothesis—particularly in view of his own comment that the time temperature curve is obviously complicated!

With regard to the two last paragraphs of Mr. Beales' criticism, it is obvious that his "Universal Negative" is tenable neither logically nor mathematically; for, granting both his postulates :—

(that $d\alpha=0$ and $KqT=$const.),

let us examine the writer's equation

$$d\alpha+KTdq=0 \quad ..... \quad (5)$$

Differentiating $KqT=$const. we get $KqdT+KTdq=0$ .... A. 2, and combining this with (5) and substituting $d\alpha=0$ we get

$$KTdq=-KqdT=0 \quad ..... \quad A. 3.$$

But in this case, either q=O or T=O, which is absurd, or T and q are both constants, so that we have successfully substituted KqT=const. in (5) and find that $d\alpha$ cannot equal O unless both T and q are constant—which they are not.

In reply to Dr. V. Henny, his remarks regarding the possibility that the formation of CO inhibited to some extent the knocking characteristics of a fuel are very interestingly supported by a recent lecture by Prof. G. I. Finch at the R.I. ("Engineering," November 27, 1931, Vol. CXXXII., No. 3437, p. 675), who put forward evidence to show that CO could and did rob oxygen from oxidised gases (*e.g.*, peroxides), it is also possible that the anti-knocking effect of enriching the mixture above the point of maximum knock may be in part ascribable to this effect.

He mentions work by Boyd which proves in fact the statement put forward in the paper in the course of discussion of Maxwell and Wheeler's flame photographs that flames were bound to accelerate in gases which are very near to their S.I.T. and would then produce vibrating flames and possibly pinking.

On an Asphalt Ring from Ur of the Chaldees.*

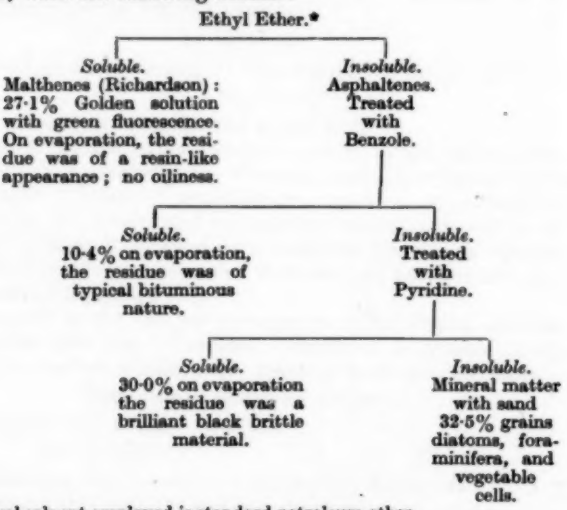
By J. E. Hackford, B.Sc., F.I.C., F.C.S. (Member), S. Lawson and P. E. Spielmann, Ph.D., F.I.C., B.Sc. (Member).

C. Leonard Woolley, excavating at Ur of the Chaldees on behalf of the British Museum and the Museum of the University of Pennsylvania, penetrated down to and below a layer of clay that has every likelihood of having been deposited by the Great Flood. Just above the Flood Layer was found the asphalt ring, the subject of the present enquiry, which may have had a date of about 3500-4000 B.C.

The shape and actual size of a portion of the ring are apparent in Fig. 1, together with the appearance of the broken ends in which fragments of vegetable matter are to be seen. The fragment weighs 3·31 g. and as it is evidently between one-half to one-third of the original object, the weight of the latter was probably about 8 g.

The freshly broken surface was friable and of a dull blackish-brown colour, and when a fragment was ground or streaked on paper it gave a chocolate-coloured powder.

A portion of the material was submitted to a series of selective solvents, with the following results :—


Ethyl Ether.*
Soluble.
Malthenes (Richardson) : 27·1% Golden solution with green fluorescence. On evaporation, the residue was of a resin-like appearance ; no oiliness.
Insoluble.
Asphaltenes. Treated with Benzole.
Soluble.
10·4% on evaporation, the residue was of typical bituminous nature.
Insoluble.
Treated with Pyridine.
Soluble.
30·0% on evaporation the residue was a brilliant black brittle material.
Insoluble.
Mineral matter with sand 32·5% grains diatoms, foraminifera, and vegetable cells.

* The usual solvent employed is standard petroleum ether.

* Paper received September 12, 1931.

Fig. 1.

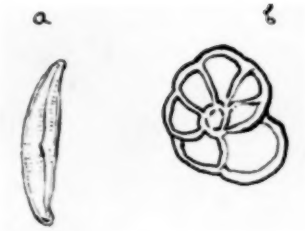


Fig. 2.

FIG. 3.

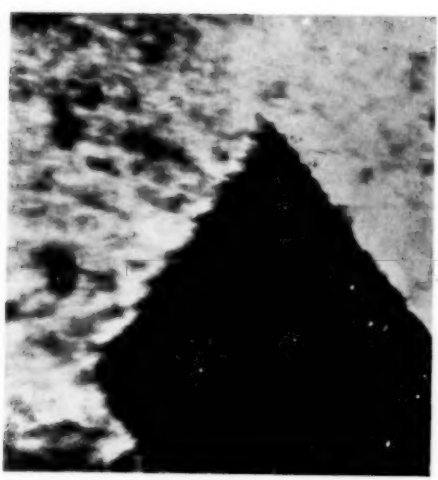


FIG. 4.

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A chemical examination of the material gave the following results :—

	Per cent.
Bitumen, soluble in pyridine	63·7
Ash, intrinsic in the soluble bitumen	3·8
	67·5
Ash, insoluble in pyridine	27·4
CO_2, equivalent to CaO in ash (see below)	1·9
Vegetable matter, etc. (by diff.)	3·2
	100·0

The sulphur content determined on the total bitumen soluble in pyridine was 7·9 per cent. This is not very different from the figure—9·3 per cent.—obtained from a sample recently analysed from Qasat Ma'Moora, in Iraq.

The composition of the ash intrinsic in the soluble bitumen (3·8 per cent.) was determined spectroscopically (by Dr. S. Judd Lewis), and was found to contain :—Ag, Al, B, Ba, Ca (much), Cb(?), Cr (substantial), Fe (substantial), K, Li, Mg, Mn, Mo, Na (substantial), Ni, Pb, Rb(?), Si (much), Sr, Ti.Tl, V and Zn.

The mineral matter (27·4 per cent.) of the asphalt ring, taken for analysis, was obtained by ashing the pyridine-insoluble matter. It consisted of :—

	Per cent.
Insoluble siliceous matter	51·3
Fe_2O_3 and Al_2O_3..	7·3
$CaSO_4$	34·2
CaO	7·1
V_2O_5	0·16
Ni (calculated as metal)	0·014
	100·074

Before ashing, the pyridine-insoluble material was found, on microscopical examination, to contain much sand, some diatoms, two types of foraminifera and well preserved vegetable fibres (Figs. 2 and 3). After ashing, the most obvious objects, apart from sand grains, were the siliceous skeletons of the vegetable fibres (Fig. 4).

The vegetable matter, 10 mm. and more in length, was found distributed throughout the mass of the ring. These fragments were obtained for microscopic examination by two different methods. In the first, the asphalt was softened by means of oil of eucalyptus, and the vegetable fragments were dissected out with fine needles, whereby undistorted specimens were obtained. A previous attempt to dissolve away the bitumen by means of warm benzole led to the disintegration of the fibrous material.

In the second method, the pyridine-insoluble matter after removal of the pyridine by means of chloroform and ether, was then mixed with an aqueous solution of erythrosine, which resulted in the lighter material floating to the surface of the water and, at the same time, the vegetable matter becoming stained with the dye. The dyed material was instantly recognisable under the microscope, and was removed with needles for examination under a higher power.

It was noticed, when a portion of the ring was heated, that the mineral matter accurately preserved the shape of the portion taken. Examination, both chemical and microscopical, shows this to consist mainly of sand and calcium sulphate, and their presence may be accounted for on a basis of observations by Mr. Woolley.

At the present time asphalt is collected near Hit as it comes to the earth's surface. Water rises with varying velocity, sometimes accompanied by so much gas that the latter will burn after being ignited. In the water are "snakes" of asphalt, which collect together and are consolidated by the natives by hand pressure into lumps, which are then thrown aside. After a very short time they become flattened owing to subsidence under their own weight. It is possible that the material was collected in the same manner in ancient times, because similar lumps of asphalt have been found at levels only slightly above that at which the asphalt ring was discovered. If this be so, it is not difficult to form a reasonable suggestion as to what occurred. The "snakes" of asphalt, in which was partially emulsified the saline water (which is usually associated with oilfields), dried in the air and under pressure, and thus received the 9·4 per cent. calcium sulphate found to-day. The mass was thrown on the ground whereby it picked up the vegetable matter and some sand; it probably received a further and intentional admixture of sand up to the 27·4 per cent. found.

It is possible, but less likely, for the calcium sulphate to have penetrated the ring subsequently to its formation. Mr. Woolley has found large crystals of selenite in damp positions at deep levels. It is well known that water can penetrate mixtures of bitumen and sand, so that it is not impossible that this has happened in the present case where the penetration has been aided by "breathing" caused by variation of hydrostatic pressure exerted by the surrounding waters.

The presence of diatoms and foraminifera does not offer much useful evidence. The former are found equally in fresh and sea-water; the latter are almost exclusively marine, but whether it is contemporaneous with the formation of the interim or is a subsequent addition, is impossible to say.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TRINIDAD BRANCH.

A General Meeting of the Trinidad Branch of the Institution of Petroleum Technologists was held at the Apex Club, Fyzabad, on April 29, 1931, the chair being taken by Mr. A. Frank Dabell.

The following papers were presented :—

ECONOMY SYMPOSIUM.

Research.

By Arthur G. V. Berry (Member).

Economy in the oil industry is allied with that agricultural problem of making two plants thrive where only one was favoured by former conditions. In other words, research is the panacea for our present troubles.

Crude oil must be converted to refined products of special value, refining processes must be brought to a high degree of efficiency, chemical treatment must be carried out with maximum economy of reagents, spent treating solutions must be regenerated and valuable compounds recovered therefrom, gasoline recovered from casing-head gas and refinery gases, sulphur recovered from the sulphuretted hydrogen, and scientific methods substituted for the rule-of-thumb methods even now so prevalent in the industry, in spite of the long period of stress through which we have passed.

The larger companies should have technical committees consisting of members of the staff capable of looking upon the several operations in a scientific manner, so that wasteful and inefficient methods can be eliminated. Smaller companies should pool their skilled resources to the same end. Each responsible official should aim at carrying out his work at lower cost, or more work at the same cost, and every man in the industry should consider how he can best co-operate with everyone else to devise new and better methods in all branches of activity.

Research is the keystone of the arch of profitable operation; conservation of resources and co-operation are the supporting pillars.

Means of Effecting Economy.

By H. A. Bennett.

Economy can be effected most profitably by eliminating waste and unproductive expenditure. Cost accounts and statistics are essential to attain this end ; the operating staff should, therefore, in times of small margins, attempt to establish closer relations with the accounting staff. Intelligent suggestions and criticisms from the operating staff will enable the accountant to produce statistics and costs which will tenfold repay the time and thought expended. Careful study of and punctuality in rendering the field returns by the operator will enable the accountant to work with less staff and complete his figures at an earlier date. The accountant also asks for bare facts ; operators should let their suggestions be considered and discard them if they are not " passed."

The popular cry in times of financial stress is " cut down overheads." Speaking technically this is " loose jargon." Overhead expenditure means expense which cannot be directly charged to a job. Very often the very existence of a company depends on an expenditure which for accounting purposes is classed as " overhead."

There is *no* security for the operator in the fact that he and his department are not overhead expenses ; he must, with the help of the accountant, get rid of waste and unproductive expense.

Sunday Labour.

By J. L. Harris.

To avoid any misconception as to the meaning, Sunday work is defined as the continuous operation of an oilfield without distinction between week-day and Sunday. An oilfield manager expressed the theory with pride by asserting that " On oilfields there are two holidays in the year—Good Friday and Christmas Day—and you work on both." The remark tritely expresses the point of view that everything is all right if all employees keep on working 12 hours a day for 365 days a year irrespective of whether their time is usefully employed or the reverse.

This is the tradition which has been handed down from those of our predecessors in the oil industry, who were almost illiterate and totally unscientific.

In the past, the staffs on oilfields tended to celebrate oilfield holidays (if any) in either a bovine or a boisterous manner. The drilling staff was rendered morose through losing its day's pay, and as oilfields were frequently operated from a driller's point of view,

it was only very rarely any holiday could be achieved. The infrequent incidence of holidays led even the most virile of the staffs to resign themselves to the treadmill which resulted in loss of initiative and output and converted an ostensible life into an unmitigated existence.

Such were the " good old times " which have been the theme of many stories, but it is asserted that nowadays all up-to-date oilfields should work as little labour as possible on the first day of the week, thereby obtaining greater contentment and efficiency in their staffs with no appreciable loss of output and a definite saving in labour costs.

Drilling on Sunday may be occasionally necessary, but as standard practice it is urged that it is uneconomical. Operations of any department on a Sunday tend to the employment of transport, machine shops and other subsidiary services.

It is consistently observed that on fields working on Sundays the day is always regarded as a period of relative leisure as far as possible, especially by higher officials in the companies concerned. A feeling of comparative lethargy pervades the lease, which results in little useful work being achieved, and the continuous employment definitely reduces the amount of work the employees do during the remaining six days.

It can definitely be asserted, from experience in the past, that Sunday labour in the period 1919-22 was a major source of waste on oilfields in Trinidad.

Even at the present time any curtailment of Sunday labour on any oilfield is bound to be economical in the long run, and executive officials following the policy advocated are in the unusual and enviable position of combining sound economy with orthodox religion and morality.

Conservation and Re-treatment of Heavy Mud.

By E. Cooper Scott, M.C., B.Sc. (Associate Member).

In broaching this subject, Mr. A. Duckham's recent paper on " The Chemical Aspects of Drilling Muds " is reiterated.

Our main object in conserving heavy mineral-laden mud is to prevent it getting so cut with gas and oil that re-treatment is a difficult or even impossible operation.

By experience, we have found that the following methods have tended to reduce costs to the extent of halving our barytes costs:—

1. When in gas, change mud at least once a day and always before coming out of the hole. This preserves the mud, and also gives a dry job pulling out.

2. When the mud is cut, circulate with plain heavy mud before putting in the barytes mud. This both washes the hole clear of any oily mud, and relieves any accumulated gas pressure. Of course this is only possible where ordinary mud will hold the gas down for a short time. A further advantage of this method is that it tends to stabilise the mud coatings on the walls of the hole. It has been found that when heavy mud is put into a well it floats off the coating of the mud which is of less dense material, with the result that gas is liberated into the heavy mud, which is consequently cut.

Most emphatic evidence of this condition has been noted during the past year.

3. Maintain circulation as constantly as possible. The most expensive operation in conjunction with barytes mud is undoubtedly coring, both because the viscosity of the mud causes slow progress, and because coming out of the hole allows gas pressure to accumulate.

4. Where possible arrange a double mud-line from the treating plant, so that old mud can be replaced by new mud continuously.

This avoids the shut down necessary when cut mud is being pumped away, and so prevents loss of drilling time when changing mud.

5. Arrange for alternative flow beans at the well, and provide ample settling pits and flow ladders. Beaning the outflow when gas is first struck prevents cutting.

6. Prevent the mud from becoming too viscous to liberate gas and to afford economical drilling.

The daily change of mud does much in this direction.

Often when drilling in shale it is found advantageous to keep a small stream of water running in the returns, preferably introduced at the pump suction, where it will mix well and will not have the effect of dropping barytes out of the mud.

7. Big pumps and fast rigs make for a saving in barytes, as they reduce drilling time.

Treating plant.—The plant consists of three 250-brl. tanks, two of which are normally used for stock and one for cut mud; the latter is fitted with a mud ladder and jets; two 10 in. by 5-$\frac{7}{8}$ in. by 12 in. pumps, capable of being compounded; one storage shed for barytes, the floor of which is at truck level, and a mixing hopper attached; one 30 ft. by 30 ft. by 8 ft. pit, for storage of drilling mud; one 10 ft. by 10 ft. by 8 ft. pit, for mixing and picking up treated and re-treated mud.

The two pits have the pumps situated between them so that mud can be picked up from either.

Deliveries from the pumps lead to the storage and treating tanks, to guns and reliefs in both pits, to the mixing hopper, and to the main delivery line.

Bottom outflows from all three tanks lead by steel ditch to the mixing pit.

This steel ditch is provided with riffles and a water jet.

It should be noticed that by this method it is necessary to set the tanks at an elevation of about two feet above the ditch.

Note.—It has been found that the 250-brl. tanks provide insufficient capacity to cope with two wells in gas at the same time. Their volume should be increased by another 500 to 1,000 brls. to cope with a three-rig drilling programme.

Treatment of the Mud.—In the weighting of fresh mud with barytes it has been found best not to use mud heavier than 70 lb. per cu. ft. as the resultant becomes too viscous when made up to 110 lb. with barytes, if a denser mud is used.

Use of oily mud must be avoided.

Treated mud should be well circulated from the storage tank to the pick-up pit before being pumped to the well, being gunned in the pit during the process.

In delivering to the well, the mud is put direct into the intake of one well pump, the other pump is thus free to pump away returning mud to the plant for re-treatment.

Re-treatment of Cut Mud.—Cut mud is circulated over a ladder, through the storage tank for cut mud, along the ditch, where it is thinned sufficiently with water to drop cuttings and knock out gas. It is then made up to weight with barytes at the hopper, and put into storage.

It is proposed at a later date to provide a large shallow pit in which badly cut mud, such as that which occurs during the bringing in of a well, may be put to be subjected to sun and rain so that the only definite leak in the otherwise continuous system may be minimised.

Economy in Drilling Time.

By G. A. Richards, M.A. (Associate Member).

It is suggested that time is the most important point for economy in oilfield work. If it is assumed for the sake of argument that it costs about $20 an hour to run a drilling rig and that, in drilling particularly, the important time is the time while the bit is actually drilling on the bottom of the hole, it must be agreed that every effort should therefore be made to reduce the time expended in other operations.

Any improvement in equipment which would lead to a reduction in the time spent on any operation will produce in the long run considerable saving of time, and therefore of money. For example, the invention of the tool-joint must have saved the industry millions of pounds sterling.

The use of hard facing materials on drilling bits makes it possible to drill with the same bit for a long period and, therefore, to save the time which would otherwise be spent pulling out of the hole, changing bits and running back again.

Powerful drilling engines and long stands of drill-pipe also save time in pulling out and running back. Another way in which some saving of time might be effected is by the use of 30 ft. lengths of casing in place of 20 ft. lengths at present used.

A further suggestion is that three or four spare bits should always be kept on every drilling well so that there would be no chance of delay while waiting for sharp bits.

Spare core barrels might also be used so that, when a full core barrel is pulled out, the empty barrel is run into the hole and, while circulating before taking the core, the full core barrel is taken apart, the core extracted, and the core barrel put together again in readiness to be run back.

It has also been stated that the use of taller derricks (about 176 ft.) has resulted in economy in drilling time on deep wells in the United States.

Of course, all these improvements and alterations have to be considered first from the point of view of whether they will pay. Improved apparatus which may not pay on a 4000 ft. well may effect a saving on a 6000 or 7000 ft. hole. The same principle applies to the use of heavy drilling engines and rigs, for the cost of transporting and the time required to set up the heavier equipment may be so great that in the case of shallow wells it may be more profitable to use lighter equipment, which may be transported and rigged up quicker, and spend an extra day or possibly more on drilling.

The underlying essential factor of economy in drilling is time.

A Factor of Economy.

By J. T. Potter.

Our company has, for many years, adopted the practice of raising derrick floors 10 to 12 ft. above ground level so as to give free access to fittings situated below the floor. A concrete floor is also provided at ground level, which is so constructed as to drain easily in one direction. It will be admitted that this is a better arrangement than having a low derrick floor with a cellar.

As the sole purpose of a high derrick floor is to facilitate the use of a blowout preventer, side-lines, etc., when drilling, on completion and thereafter for the life of a producing well, this space is unnecessary and serves no useful purpose. The well is thus left with a wooden floor and a concrete floor, either of which is available for production work.

If the wooden floor is removed soon after the well is brought into production, all flooring boards, supporting posts and four sills can be salvaged and moved to new locations until they are unfit for further use.

This alone represents a saving of approximately $200 for each well, but, quite apart from this considerable saving, also has the following advantages, all of which can be said to contribute to economy of operation and maintenance: (1) Future repair work to the original derrick floor is obviated, as it no longer exists; (2) the life of the remaining sills can be prolonged, as they are open for inspection at all times; (3) fire risk is less, as the concrete is easily washed free of oil and inflammable rubbish; (4) all production work is carried out at ground level, which reduces the risk of accidents and permits of a hurried exit if this is necessary; (5) pumping and power units can be set at ground level on permanent concrete foundations, thus freeing the derrick from all vibration.

It is, of course, necessary to leave the top of the oil-string as near as possible to the concrete floor, but, where this has not been done, the oil-string can be cut and re-threaded to bring it down to a convenient height for handling the tubing.

One important point to remember is that, as all casing and oil-string depths are calculated from the rotary table, all future measurements must also be taken from this point.

Salvage.

By H. D. Fletcher (Member).

In days of depression, such as the present, everyone looks round to see where, and to what extent, economies can be effected, and salvage is usually one of the first channels to be investigated.

When material is required for the field, the tendency is to order new in preference to looking for used material that would serve the same purpose, the result being that there is often an unnecessary accumulation of perfectly sound material lying idle until its collection and use is enforced.

Some of the items most common to abuse in this way are small valves, cocks, bull plugs, pipe nipples, packing, pipe wrenches and tongs, flanges and flanged unions, etc., the latter usually being left in halves on odd nipples of pipe.

The reason for this is generally because more than the necessary quantity has to be taken out to the job in order to save delays in long journeys back to the stores for small items.

On the completion of a job all surplus fittings should be placed on the roadside where they can be seen, not thrown in the grass to be overgrown, and arrangements made for vehicles, when passing, to collect and take them to a central depot, such as a field tool shed or salvage dump.

Other instances where salvage can generally be effected are: (1) Where finished wells can be pumped and cleaned out from the ground level, the derrick flooring, floor sills, props and steps, etc., can be removed and used in derricks for drilling new wells; (2) production strings and casing can, where permissible, be profitably cut and recovered from wells that have declined to a low figure of production; (3) considerable salvage of line pipe and fittings can often be effected without much labour by the rearrangement of pipe-line systems as development extends from one area to another; (4) expensive high pressure fittings should always be recovered from new wells as soon as the pressure has dropped sufficiently to permit them to be dispensed with or replaced by similar fittings of lower pressure and less cost; (5) road metal can be recovered from obsolete roads for use elsewhere.

The institution of a special salvage department for this work is not recommended, as that is unnecessary and is generally nothing more than an additional expense.

Salvage departments usually collect everything they see lying about, not knowing whether it has been placed there for a specific purpose or not. By this means they try to show a satisfactory return as a department, but in doing so defeat their own object and give endless trouble to the departments whose materials they remove.

The proper control for salvage work is the head of the department to which the material belongs.

Casing.

By L. A. Bushe (Member).

A good deal has been said, and written, recently on the standardization of tubular goods in Trinidad, and the difficulties of standardizing on sizes and weights of casing in a place where the conditions are so varied are fully appreciated. It is felt, however, that more attention might be paid to the depths at which it is safe to set pipe in the different fields, having regard to safety margins or factors of safety which should be applied to strings of casing used on various jobs.

Safety factors of either 2 or 2½ are commonly used for the collapsing depths of casing, and this is very sound practice where it is the intention to lower the fluid level in the pipe, thereby exerting pressure on the casing wall. In some cases, where several strings of casings are set in a well, the fluid is only lowered for the purpose of testing the shut off. It is obviously unnecessary in these instances to apply high safety factors to the setting depth. As long as the petroleum technologist does not insist on the fluid level being bailed below the point at which the factor of safety would apply, it would be possible to set the casing at the actual collapsing depth of the pipe.

In the U.S.A. to-day strings of casing are being set at depths almost as great as the collapsing depths of the pipe used without any factor of safety, a recent publication showing that 13⅜ in., 68 lb. grade D casing was lowered to 6766 ft., and 9⅝ in. 40 lb. pipe of the same grade to 6498 ft. Although there is some difference of opinion regarding the actual collapsing depths of these strings, there is no doubt that the figures are very close to those given above.

It is to be regretted that more information is not available at the present time as to the collapsing values of seamless casing, but it is hoped that this will soon be rectified, as the A.P.I. Committee on Pipe Standardization, realizing the importance of the question, have asked for a sum of $10,000 to be spent in making tests in order to establish the proper values.

It is not suggested that individual operators in Trinidad should carry stocks of pipe of the same size, but of different weights for use on a variety of jobs. This would only lead to confusion. But several weights of some casing sizes are already in the island, and it is thought that there would be a definite saving if, when the occasion arises, more purchasing were done between companies—always provided that the selling company was prepared to sell without making a profit. In this way it would be possible for an operator to buy the exact amount of casing required for the job in hand, and he would obtain the advantage of occasionally being being able to use a lighter, and therefore cheaper, pipe than he carries in stock.

Coring is Cheaper than Drilling.

By C. C. Wilson, A.R.S.M. (Associate Member).

These remarks are put forward on account of the fact that in the cause of economy coring tends to be neglected.

The objects of coring are: (1) To obtain stratigraphical and structural evidence for the determination of marker horizons and

thus for correlation with neighbouring wells and outcrops; (2) To examine the percentage of porous oil-bearing formations within the series drilled; (3) to obtain definite information regarding the positions of dangerous water-bearing formations and their lateral extent.

In regard to correlation it is well-known in the south western oilfields of Trinidad that, as in oilfields all the world over, it is *absolutely* necessary to know the position of at least one marker horizon —*e.g.*, the base of the Forest Clay or the top of the Cruse.

Without this information it would be essential, on the irregular flanks of Trinidad structures, to set casing deeper than necessary to cover unknown watered zones, and thus to restrict the thickness of available producing zones.

Turning to the oil zones themselves, and taking the extreme case, even assuming that the stratigraphical position of the well is known, it is quite possible that *no* commercial horizons may have been penetrated on reaching the calculated depth. If no coring has been done, this would not become apparent until time had been wasted in the fitting of connections, running tubing and washing.

If coring had been carried out, the barrenness of the beds would have been apparent and the well carried deeper until commercial oil had been met, with no loss of drilling time.

The system of running perforated casing into the uncased part of a well is bad and unscientific on account of: firstly, sloughing in of unconsolidated clay zones and the resultant necessity of continual cleaning; and, secondly, the occurrence to a greater or less degree in every oilfield of so-called thief sands which absorb production from the well; if the position of these were definitely known (as by coring), blank pipe could be inserted to cover these sands.

Again, some sands at the top of the Cruse zone at Palo Seco contain high pressure gas with very little oil, if these sands were partially shut off by using blank pipe, this pressure could be used for lifting power. This, again, could only be done with assurance on the results of coring.

Regarding the watered zones in a well, it has been shown repeatedly that no individual oil zone is absolutely free from water. Some time or another a well is drilled into a new water sand within oil formations previously supposed to be water-free. By knowing the exact positions of watered zones it is possible considerably to extend the producing thickness in any well, and, by proving the absence of water, one might be able to cut down the quantity of cement instead of insisting invariably that cement be carried back to the base of the forest clay.

During the discussion on Mr. Duckham's paper on "The Chemical Aspect of Drilling Muds," it was suggested that rock fragments from a high-pressure zone do not give up free gas until after being carried upwards by the mud to a point where the weight of the mud column is sufficiently reduced to allow of its release. In coring, almost the whole of the cut rock is enclosed in the core barrel, and gas is released only when the barrel is opened on the derrick floor. Coring, therefore, reduces instead of increases the risk of blow-outs.

It is generally believed that the time necessary for coring makes the process almost prohibitive. From statistics it is apparent that coring time is, on the average, less than double that taken by straight drilling, so that in the drilling of an average well fourteen days would be about the extra time needed for coring—*i.e.*, a delay (not a loss) of fourteen days production, say 3000 to 6000 brls. per well. With regard to difficulties arising from coring in pressure zones, the use of sodium silicate after the casing had been set, facilitates the use of heavy muds, thus holding the well under control.

The only really serious factor at the present stage and apparent costliness of coring is *time*—and delay of production.

One well lost through neglect of coring would mean the loss of more money than the extra expenditure of coring 10 wells.

In addition to this, enhanced production and longer lives of wells, which might be obtained by judicious casing programmes based on coring, together with a complete control of water conditions would cover any losses resulting from the loss of time.

Core Samples.

By P. W. Jarvis.

It is not usually realised what a vast amount of evidence can be obtained from core samples. The dip and strike of the strata can frequently be noticed, and its lithology, whether it is a clay, sand, shale or sandstone. Traces of oil or lignite are quickly seen and sometimes a large shell or a sea-urchin is found. The most important evidence, however, is the abundance of small fossil foraminifera.

The majority of core samples contain these fossils, and by their aid it is possible to show the age of the bed through which the drill is passing. One can correlate it with the same bed in other wells, and also with surface exposures, because every bed contains its own particular assemblage of fossils.

It must be admitted that these fossil foraminifera are small; but this defect is more than compensated for by the vast numbers in which they occur and by their excellent preservation.

There is a company in Venezuela which insists on a piece of every core sample taken being sent to their Maracaibo office, where the fossils are extracted, mounted and carefully recorded, with most valuable results.

The majority of core samples taken in Trinidad are not examined for fossils.

From the examination of the fossils from core samples it has been possible to show that in one well the drill had passed from the Middle Miocene through an unconformity into the Cretaceous. In another well it passed into the Eocene, and in a third into the Oligocene, thus establishing a previously unknown unconformity under the producing field.

Salvage and Reconditioning of Material.

By A. J. Ruthven-Murray, M.A., B.Sc., F.G.S. (Member).

All operating oilfields should have a Salvage Department, its objects being: (1), to collect all material no longer in use or likely to be used in its existing position; (2), to transport such material, if in good condition, to the warehouse for re-issue or if otherwise, to the Repair Depot for overhaul; (3), to re-condition material brought in and, after being inspected and tested, return it to the warehouse for re-issue.

Almost every class of oilfield material can be profitably dealt with by the Salvage Department, but the materials most generally handled are pipe and pipe fittings.

The Repair Depot should form an annex to the Field Machine Shop and should be provided with the following equipment: Hydraulic Pipe-straightening Machine; Pipe-threading Machine; Work Benches equipped with vices and small tools; A large Metal Tank for cleansing all fittings of oil and tenacious foreign matter. This should be equipped with a steam coil in the bottom for heating the cleansing liquid. The liquid usually employed for this purpose is a solution of caustic soda or "Oakite" in water, but there are several proprietary compounds on the market suitable for this purpose. This tank should also have a loose steel cage or basket to receive all small fittings, valves, unions, tees, etc., which are to be cleansed. Above the tank is arranged a chain hoist and runway so that the cage, when loaded, may with ease be lifted, conveyed and lowered into the cleansing tank; Hydraulic Test Pump for testing valves, unions, etc., under pressure; A small Lathe is a

useful adjunct, but not essential, as the amount of turning required is comparatively small, and this can be undertaken by the Machine Shop.

The Department should be provided with a large number of partitioned shelves and bins for the storage of sound component parts, of which there will always be a number on hand which can be added to other sound but different components to make valves or other items of equipment fit for use. For instance one half of a union may be in good condition, the other half useless; but shortly there comes along another union with the opposite half in good condition and a complete article is thereby obtained, which after testing is ready for re-issue.

Suitable space should be provided at one end of the building and alongside the road for the dumping, breaking-down and sorting of salvaged material. There should also be pipe racks situated parallel to the road and parallel to the Pipe-straightening and Threading Machines. An overhead hoist and runway should be provided for conveying pipe from the racks to the above mentioned machines.

So soon as a well ceases to be a commercial producer, it is placed on the drilling programme either for deepening or abandonment; if for the latter, then so soon as abandonment is completed, all pipe-lines connected therewith are lifted and the material placed on the roadside convenient for transport to the warehouse or Salvage Department according to condition.

Bad pipe is straightened or re-threaded as the case may be and then returned to the main racks for re-issue. Fittings are all disconnected, cleansed and sorted into their various classes.

The operators of the Department then handle material in a batch. For instance all will concentrate upon the reconditioning of tees; the threads are carefully examined and tested, any bad ones being sent to the scrap heap. The reconditioning of elbows, tees and unions is simple and speedy, but valves take up a large portion of the Department's time.

Expensive valves can be made equal to new at small cost by fitting new seats, discs or clacks. These replaceable parts are stocked in the warehouse for issue to the Salvage Department as required.

When drilling machinery has been moved away from a well to a new location, there is usually a certain amount of material for the Salvage Department to sort and re-condition. Apart from fittings, there are bent bolts to straighten, nuts and washers to collect and return to stock.

Construction material such as timber and galvanised iron is collected and sorted, to be used again in preference to calling for the issue of new material. Galvanised iron which has been removed from

roofs of buildings on account of a few leaks can be used for enclosing the standard tool end at wells, or flattened out and used for core-trays.

Orders for material from the Field must be taken to the Salvage section of the Store from which re-conditioned material must be issued if in stock ; if not in stock the order is stamped accordingly with a rubber stamp and then, and then only, may new material be issued.

The operators in the Salvage Department need only be semi-skilled.

An hydraulic test pump can easily be constructed by taking the hydraulic pump from a Watson Stillman Casing Jack. This will give a pressure of 2,000 lbs. per sq. in.

False Economy.

By A. F. DABELL, M.I.Mech.E. (Member).

It is necessary over all to remember that if the practice of true economy be a virtue, that of false economy is a vice.

It is known to many that the wasteful gas-oil ratio is not necessarily improved by reducing the amount of oil released ; the converse often applies.

Similarly, the drilling of small cheap wells of low yield has led to disaster where a bolder policy of deep drilling would have resulted in success.

There are some who consider that economy may be effected only by reduction of expenditure, with the result that the industry becomes merely a carcase upon which to operate when judicious increase in expenditure might lead to success.

In short, economy should be prompted by a policy of courage and prudence rather than cowardice.

DISCUSSION.

Mr. Van Achterbergh emphasised the necessity of keeping statistical and graphical records in order that a clear survey could be made at any time in regard to a company's operations.

Mr. L. A. Bushe said that he did not agree with the idea of having a separate Salvage Department, but thought that the head of every department should do the salvage work required. He knew of a case where the salvage gang used to go round and

take the crown block pulleys from wells, thinking they were effecting a saving. As Mr. Fletcher pointed out, it should be the business of the head of the department to go round and carry out what salvage was necessary in that department.

Mr. C. E. Capito said that when they did use lighter pipe he thought they probably would not really get much economy in the end. They might save $2,000 or $3,000 on the initial cost of the well when they had a high oil level and a fair gas pressure, but once that oil level and gas pressure decreased and the well had to be put to pump and the level fell below the depth of the factor of safety they immediately got into a dangerous state and which was occurring in a large number of cases.

The question of cement was not very expensive and it saved casing when they started to reduce the fluid level in the well. Given a good ring of cement round the casing there was less chance of it collapsing. How were they going to shut off their watersands if they did not use cement? His department never asked anybody to cement right up to the top of the well, but this was done in Persia from the point of view of corrosion.

He endorsed Mr. Harris' paper, and Mr. Potter's idea of keeping casing-head fittings as low as possible. The higher casing-head fittings were put the more chances there were of damage. In Persia they always put their casing-head fittings as near the ground as possible so as to prevent any bending movement should a pipe break when connected to a high-pressure well.

On the question of salvage he desired to endorse Mr. Bushe's remarks on that. He had a similar case, and it was necessary for the heads of department to race round and see what the salvage man was doing, otherwise he was liable to remove a fitting that was lying on the road in the endeavour to make his department pay regardless of what delays he caused.

Mr. Fletcher stated that, with regard to the collapsing depths of strings of casing, he thought that in some of those depths quoted by the Americans they must have been considering the level to which they brought their cement up in the hole, otherwise they could never set their strings of casing to those depths with any degree of safety. He thought they drilled a bigger diameter hole, which gave a bigger annulus to be filled by cement, and they took that into account in figuring their collapsing depths.

Mr. A. H. Richard agreed that the Salvage Department by itself was not economical, as, by itself, it could not possibly know the potential uses of equipment which was left lying about, and would spend more money than it saved.

Further, he ventured to suggest that the subject of economy was intimately bound up with common sense. He did not wish to appear to detract from the merits of any of the papers read that evening, but he thought that they were only of limited value, because one could not lay down hard and fast rules on methods of economy. They could give facts and describe methods that have been adopted in other cases and proved successful, but that was as far as they could go.

In dealing with a scientific subject, the setting out of facts, laws or principles which had been established in the past was essential, to serve as stepping stones without which later workers could not advance to further discoveries and achievements. If, however, a man was told that a certain procedure had produced best results at lowest cost in a specified instance, unless that man had common sense, he would not be capable of modifying what he had been told to apply to other conditions. Each problem had to be tackled on its own merits, and the ability to do so was a quality which either came naturally to a man or not at all. In the latter case, no amount of relation of past experience of others would be of any avail.

It was his opinion that that concern, in whatever industry it might be engaged, would achieve economical operation, which was essential to success, which employed a staff possessing sound judgment and common sense.

Mr. A. Chadwick agreed with Mr. Murray in that a salvage department was very necessary. For each individual department to handle their own salvage meant duplication of both men and materials and unnecessary expense. Furthermore, the reconditioning of materials and fittings should be carried out, if not by the field machine shop, then in conjunction with the shop, so that machine shop equipment could be utilised.

Mr. G. H. Scott said that many of the papers that night were not based truly on principles of economy but in some part on the pet theories of the various authors.

He wished Mr. Van Achterbergh had emphasised a little more the advisability of keeping adequate records. Without adequate records he did not consider that there could be a true gauge of economy. Statistical records of all kinds would, in his opinion, give them a good idea as to where economies could be instituted and what economies had been effected.

Mr. J. L. Harris said that the question of salvage was a much debated one, and he thought in the present circumstances it was not advisable to have a separate salvage department. Salvage,

on most fields, was usually mainly attributable to one particular department, and he might say that from personal observations he inferred that the drilling department was often the chief offender. If the drilling superintendent was keen on minimising salvage, then the salvage was good; if there was wastage in the drilling department, then salvage was abnormal. If a separate department was unavoidable, he thought the man in charge should be possessed of sound judgment.

Regarding the point brought up by Mr. Scott about statistics he agreed with him, and he would like to stress the fact, that a good statistical department on any field would enable very great reductions to be made in the staff of accountants on that field. Marked economies would then be effected and infinitely more valuable data produced.

Mr. A. J. Ruthven-Murray said that he regretted that so many people had had such bad experience of salvage departments. It was clear that the salvage departments of which they had personal knowledge were without organisation and completely lacking in supervision; this is proved upon reference to the removal of crown blocks from derricks. It is essential to have departmental co-operation if a salvage department is to be run efficiently. It was his idea that each department would collect together its own salvage material ready for transportation. Field engineers would look after pipe-lines, take them up when no longer required and have the material laid on the roadside, ready for removal by the transport department when trucks are passing by empty, or during slack periods. The drilling department, when they complete or abandon a well, collect together all damaged or unserviceable material and this is sent in to the salvage department for overhaul. Every field should have its salvage department, so that all unserviceable material could be sorted and either relegated to the scrap heap or reconditioned and put back into service, so effecting a considerable saving by cutting down the quantity of new material ordered.

He did not intend, as appears to be thought by some speakers, that each department should have an officer looking after the work of salvage alone, but that each department should be responsible for the salvage of its own material.

In connection with Mr. Richard's paper, the circulating of wells may be considered one of the largest factors in the expenditure of unproductive time. Anything that can be done to bring about a time reduction in this operation would be valuable, and the use of large pumps has so far been of the greatest assistance in this direction.

The Chairman (Mr. A. Frank Dabell) suggested that the contention of Mr. Wilson that the cost of coring was less than double that of straight drilling could not be upheld.

It was common practice to drill 300 ft. per day at 3000 ft. depth, whilst it is doubtful if 100 ft. could be cored in the same period. In addition, coring the same distance entails a five times increased wear and tear upon tool-joints, ropes, tongs, plant, etc., apart from increased power consumed.

The cost of coring must be something like ten times that of straight drilling, with time valued commercially.

The Chairman closed the meeting by proposing a vote of thanks to their hosts, the members of the Apex Club, for the use of the room.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS

TRINIDAD BRANCH.

A GENERAL MEETING of the Trinidad Branch of the Institution of Petroleum Technologists was held at the Apex Club, Fyzabad, on January 28, 1931, when the chair was taken by Mr. A. FRANK DABELL.

A paper on "Standardization in Drilling and Well Pumping Equipment" was read by Mr. R. N. Kirby (Associate Member), and dealt in particular with the specifications of the American Petroleum Institute. The author concluded that standardization is sound in principle and not difficult or costly in operation if the economy and efficiency derived thereby is fully considered.

The subsequent discussion was taken part in by Messrs. A. Frank Dabell, J. M. Penney, E. G. Rooks, W. J. C. Cooke, B. M. Grover, P. Kummer, E. Poupart, Col. H. C. B. Hickling, H. D. Fletcher, C. E. Capito, R. P. Homan, L. A. Bushe, A. H. Rose-Innes and L. J. Wilson.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TRINIDAD BRANCH.

A GENERAL MEETING of the Trinidad Branch of the Institution of Petroleum Technologists was held in the Trinidad Leaseholds Club, Fyzabad, on November 26, 1930, Mr. A. FRANK DABELL in the chair.

A paper in "Detonation in Internal Combustion Engines" was read by Mr. A. P. Chamberlain, B.Sc. (Student), and a discussion followed in which Messrs. A. Frank Dabell, W. Malcolm Brown, L. J. Wilson, and Neils Matheson took part.

CURRENT PETROLEUM NOTES.

Industrial Alcohol in South Africa.—A company is proposing to manufacture motor fuel and other by-products from the surplus maize production in the Union of S. Africa. There will ultimately be ten factories producing alcohol and products, and the scheme is said to have the approval of the Government. Fifty per cent. of the moter will be blendable with the imported product, and it is understood that legislation has been promised to make blending compulsory and to fix the price of motor spirit.

New Alberta Oilfield.—The possibility of a new oilfield in Southern Alberta is indicated by reports that the Keho No. 1 Well of the Hudson's Bay Oil and Gas Co. has struck oil, and a flow of gas estimated at 750,000 cu. ft. per day, in the Madison limestone at a depth of 4925 ft. This well is about 18 miles N.W. of Lethbridge and was started in April, 1930. At 3700 ft. a good show of oil was obtained in the Benton formation, yielding 50 to 60 brls. per day.

REVIEW.

PÉTROLES NATURELS ET CARBURANTS DE SYNTHESE. Constitution Chimique-Traitement Utilisation par Andre Graetz. Paris: Librairie J. B. Bailliere et fils, 19, Rue Hautefeuille, 19, 1931.

This excellent monograph by one of our distinguished French members fills a definite gap in the literature of petroleum.

In a characteristic preface Mons. P. Dumanois points out the importance of a truly scientific outlook in industry, and the real necessity of collaboration between the chemist and the engineer in the great field of petroleum technology. He says for example :—

"Trop souvent les ingenieurs mecaniciens ont consideré que l'etude du moteur relevait de la thermodynamique pure en oubliant que le phenomene de combustion etait un phenomene chimique profondement complexe."

And again :—

"Dans un domaine ou l'empirisme faisait trop souvent loi, il a voulu introduire l'esprit scientifique. Les hypotheses et les deductions personnelles, discutables comme toute hypothese ou toute deduction, donnent au livre un attrait tout particulier. Enfin l'ouvrage comporte une documentation et une bibliographie de premier ordre, particulierement precieuse pour les techniciens auxquels il s'adresse."

The scope of this work is briefly exemplified in the following survey: The first part contains chapters devoted to the production of petroleum, its constitution and its chemical and physical properties. The action of a variety of reactants on hydrocarbons is fully dealt with.

The identification and separation of the various series of hydrocarbons is discussed, and there follows a series of chapters concerned with the general methods of refining of gasoline, kerosine and lubricating oils.

A very full section is occupied by the development of the theory and practice of cracking, and no less than 140 pages are devoted to this subject in its various aspects. Hydrogenation, both of coal and petroleum residues, is briefly discussed, and a very excellent summary is given of synthetic carburants originating from methane, ethylene, acetylene and water gas. The last chapters deal with the utilisation of petroleum products in the internal-combustion engine.

Altogether this work can be highly recommended. It is written in an admirably clear and concise way and does every credit to the author.

A. E. DUNSTAN.